43380

24,3200

S/056/62/043/005/046/058
B125/B104

AUTHORS: Komarov, L. I., Fisher, I. Z.

TITLE: On the theory of the Rayleigh scattering of light in fluids

PERIODICAL: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 43, no. 5(11), 1962, 1927 - 1933

TEXT: A molecular theory of the intensity and spectrum of the Rayleigh scattering of light in liquids or dense gases is formulated without using the thermodynamical theory of fluctuations. This paper is a transcript of one by L. Van Hove (Phys. Rev., 95, 249, 1954) from the "language" of scattering of neutrons to the "language" of scattering of light. N is the number of molecules contained in the volume V and $R_i(0)$ $(i = 1,2,\dots,N)$ indicates the position of the particles at a certain initial moment, $R_i(t)$ is their position at a later moment. The spectral density

$$I'(\mathbf{R},\omega)=\frac{\alpha^2\omega^4 N}{2\pi c^4R^2}I_0\sin^2\gamma\int\limits_{(V)}d\mathbf{r}\int\limits_{-\infty}^{\infty}dt\,\times \quad (21)$$

$$\times\exp\left\{i\left(\mathbf{k}_0-\frac{\omega\mathbf{R}}{cR}\right)\mathbf{r}-i\,(\omega_0-\omega)\,t\right\}G(|\mathbf{r}|,t),$$

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of the intensity of the scattered light is a Fourier transform of a space-time molecular Van Hove function $G(|\vec{r}|,t)$ of the scattering system. $\cos\gamma = |\vec{E}_0\vec{R}|/R|\vec{E}_0|$; I_0 and $\vec{E}_0$ are the intensity and the electrical vector of the incident radiation. $G(|r|.t)$ is (with an accuracy up to the coefficient N^{-1}) the density of the relative probability of finding a certain particle, at the instant t, at a distance $\vec{r}$ from the initial position of any given particle in the system. After scattering through the argle of 0^{o} has been excluded, G has to be replaced by G-1. The integration over $d\vec{r}$ can be extended over the entire space. Eq. (21) then leads to the formula

$$I'(\mathrm{R},\omega) = \frac{2\alpha^2\omega^4 N}{c^4R^2} I_0 \sin^2\gamma \int_0^\infty r^2\,dr \frac{\sin\varkappa r}{\varkappa r} \int_{-\infty}^{\infty} dt\,(G(r,t)-1)\,e^{i\Omega t}. \quad (25)$$

or, with $G(\vec{r},0) = \delta(\vec{r}) + g(|\vec{r}|)/v$, to the formula

$$I'(\mathrm{R},\omega) = \frac{\alpha^2\omega^4 N}{c^4R^2} I_0 \sin^2\gamma\,\delta(\omega-\omega_0) \left\{1 + \frac{4\pi}{v}\int_0^\infty (g(r)-1)\frac{\sin\varkappa r}{\varkappa r} r^2 dr\right\}. \quad (27).$$

In contrast to the static theory, the present dynamic theory yields a certain definite spectrum of the frequencies in scattering. The formulas

(25) and (27) yield equal intensities of the scattered light (aside from corrections of the order of $(v/c)^2$). The polarizability of one molecule in the field of the neighboring molecules is therefore $\alpha = v^2(-\partial\varepsilon/\partial v)_T/4\pi$, where ε is the dielectric constant. Up to now, the spectrum of scattered light cannot be calculated from formula (25).

ASSOCIATION: Belorusskiy gosudarstvennyy universitet (Belorussian State University)

SUBMITTED: June 19, 1962

S/053/62/076/003/003/005
B125/B102

AUTHOR: Fisher, I. Z.

TITLE: Present stage of the theory of fluids

PERIODICAL: Uspekhi fizicheskikh nauk, v. 76, no. 3, 1962, 499-518

TEXT: On the basis of papers published from 1935 to 1962 a short survey is given on the present stage of the statistical theory of ordinary fluids with restriction to the classical theory. According to the opinion of the present author, the modern development of this theory was initiated by Yakov Il'ich Frenkel'. There are 1 figure and 46 references: 18 Soviet and 28 non-Soviet.

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ZAYTSEVA, A.M.; FISHER, I.Z.

Motion of hydrated ions in solutions. Zhur.strukt.khim. 4 no.1: 3-9 Ja-F '63. (MIRA 16:2)

1. Beloruskiy gosudarstvennyy universitet.
(Electrolyte solutions) (Ions--Migration and velocity)

ZATYSEVA, A.M.; FISHER, I.Z.

Effective mass of a hydrated ion in solution. Zhur.strukt.khim. 4 no.2:173-175 Mr-Ap '63. (MIRA 16:5)

1. Belorusskiy gosudarstvennyy universitet, Minsk.
(Ions--Migration and velocity) (Hydration)

ZAYTSEVA, A.M.; FISHER, I.Z.

Mobility of hydrated ions. Zhur.strukt.khim. 4 no.2:261-262 Mr-Ap '63. (MIRA 16:5)

1. Belorusskiy gosudarstvennyy universitet, Minsk.
(Hydration) (Ions--Migration and velocity)

FISHER, I.Z.; ZAYTSEVA, A.M.

Effect of the hydration of ions on the viscosity of electrolyte solutions. Zhur.strukt.khim. 4 no.3:331-335 My-Je '63.
(MIRA 16:6)

1. Belorusskiy gosudarstvennyy universitet, Minsk.
(Electrolyte solutions) (Hydration) (Viscosity)

FISHER, I.Z.; ADAMOVICH, V.I.

Density fluctuations in water. Zhur.strukt.khim. 4 no.6:819-823 N-D '63. (MIRA 17:4)

1. Belorusskiy gosudarstvennyy universitet.

ACCESSION NR: AP4000411 S/0046/63/009/004/0427/0433

AUTHORS: Kacharskaya, L. V.; Komarov, L. I.; Fisher, I. Z.

TITLE: Hypersound and slow neutron scattering in liquids

SOURCE: Akusticheskiy zhurnal, v. 9, no. 4, 1963, 427-433

TOPIC TAGS: hypersound neutron wave diffraction, liquid hypersound neutron wave diffraction, high frequency hypersound, hypersound neutron scattering, slow neutron scattering, hypersound slow neutron scattering, hypersound neutron scattering spectrum, hypersonic radiation, neutron scattering, neutron, scattering, hypersound

ABSTRACT: The conditions leading to neutron wave diffraction on hypersounds in liquids are analyzed, and conditions for building an experimental apparatus specified. Slow neutron scattering is found to be the most suitable because of the requirements of very high frequencies for the determination of hypersounds in fluids. The expression for the neutron energy E and momentum p during and after the scattering is represented by

$$E - E_0 = \pm u(\Omega)\,|\mathbf{p} - \mathbf{p}_0|,$$

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where $u(\Omega)$ can be calculated by experimentally determining p or E. For small scattering angles Θ and small values of $\Delta E/2mu^2$ this expression is written in the form

$$\Delta E \approx \pm \frac{2E_0 \sin\theta}{\sqrt{\frac{2E_0}{mu^2}-1}}.$$

The discussed neutron diffraction characteristics are shown to have no analogies in optical theory, with auxiliary peaks in the neutron spectrum at zero angle neutron scattering. This effect may yield direct information experimentally on hypersounds in the limits of high frequencies. Orig. art. has: 30 formulas and 1 figure.

ASSOCIATION: Belorusskiy gosudarstvennyy universitet, Minsk (Byelorussian State University)

Card 2/3

ADAMOVICH, V.I.; KUNTSEVICH, I.M.; FISHER, I.Z.

Short-range order near an excited molecule in a liquid. Zhur. fiz. khim. 37 no.11:2568-2570 N'63. (MIRA 17:2)

S/056/63/044/002/025/065
B102/B186

AUTHOR: Fisher, I. Z.

TITLE: Localized excitons in fluids

PERIODICAL: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 44, no. 2, 1963, 541-547

TEXT: The author develops a hydrodynamic theory for the motion of a localized exciton, considered as a quasiparticle, in a fluid. The localized exciton, which in the microscopic theory is considered as a specifically ordered region in the neighborhood of an electron-excited molecule moving along the exciton, is regarded in the hydrodynamic theory as a small dense region in the fluid. The only assumption made is the necessity for such conditions that a localized exciton is not only produced but also conserved for a sufficiently long period. The above-mentioned dense region is characterized by $\varrho(\vec{r}) = \varrho_0 \exp\left[-\vec{\Psi}(\vec{r})/kT\right]$ where ϱ_0 is the normal density and $\vec{\Psi}(\vec{r})$ is the mean selfconsistent force potential, considered as given, and $\Psi(\vec{r}) = \Psi(|\vec{r}|)$. The force acting around the center of the exciton is

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given by $\vec{K}(\vec{r}) = \frac{1}{\varrho}\nabla p = -\frac{c^2}{kT}\nabla\bar{\Psi}(|\vec{r}|)$ (per mass unit); p is the pressure and $c^2 = (\partial p/\partial\varrho)_T$. For an ideal fluid

$$\rho(r) = \rho_0 \exp\left\{-\frac{\bar{\Psi}(|r|)}{kT} + \sigma(r)\right\} \quad (3)$$

$$K(r) = -\frac{c^2}{kT}\nabla\bar{\Psi}(|r|) + c^2\nabla\sigma(r). \quad (4).$$

Since the kinetic energy can be set up as $E_{kin} = \frac{1}{2}\int\varrho(\vec{v}-\vec{U})^2dV \approx \frac{1}{2}\varrho_0U^2\int(\nabla\varphi)^2dV$, the factor multiplied by $U^2/2$ can be taken as the effective mass. The motion is considered in a system in which the exciton center is at rest, i.e. the fluid has a stationary flow with the velocity $\vec{U}$ at infinity; $\vec{v} = \vec{U} + U\nabla\varphi(\vec{r})$, $\Delta\varphi = \frac{1}{kT}\bar{\Psi}(r)\cos\theta$, $\bar{\Psi}(r) = \begin{cases}\varepsilon(r/R-1) & r<R\\ 0 & r>R\end{cases}$. One obtains $M_{eff} = \frac{2\pi}{15}\left(\frac{\varepsilon}{kT}\right)^2\varrho_0R^3$, or, if the total mass in the sphere of radius R is $M = 4\pi\varrho_0R^3/3$, $M_{eff} = \frac{1}{30}(\varepsilon/kT)^2M \ll M$. Subsequently the exciton motion is investigated for a viscous fluid. The characteristic length

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$L = \frac{U}{\varphi_0 c^2}(\frac{4}{3}\eta + \zeta)$ takes displacive (η) and volume (ζ) viscosity into account.

$$\varphi(x, y, z) = \sum_{n=0}^{\infty} (-L)^n \frac{\partial^n \varphi_0}{\partial z^n}. \quad (24)$$

will be a solution of the kinetic equation

$$\Delta\left(\varphi + L\frac{\partial\varphi}{\partial z}\right) = \frac{1}{kT}\frac{\partial\overline{\Psi}}{\partial z}, \quad (20).$$

For small but finite L, $\varphi(x,y,z) \approx \varphi_0(x,y,z-L)$. When energy dissipation due to viscosity is taken into account, the exciton is subjected to the frictional force $\vec{F}_{fr} = -h(-\vec{U})$, where $(-\vec{U})$ is the velocity of an exciton whose coefficient of friction is

$$h = \int\left[2\eta\left(\frac{\partial^2\varphi}{\partial x_i \partial x_k}\right)^2 + \left(\zeta - \frac{2}{3}\eta\right)(\Delta\varphi)^2\right]dV. \quad (27).$$

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Localized excitons in fluids

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For slow motions:

$$h = \frac{4\pi}{9}\left(\frac{59}{60}\eta + \zeta\right)\left(\frac{\varepsilon}{kT}\right)^2 R. \quad (29),$$

which, compared with the Stokes law $h = 6\pi\eta R^*$, yields the inequality $R^* \ll R$; R is the effective radius of an exciton considered as a hard sphere and R is the linear dimension of the region occupied by the exciton. The relaxation time in the case of translational motion can be estimated from $\tau = M_{ff}/h$, and the diffusion coefficient from $D = kT/h = kT\tau/M_{eff}$.

ASSOCIATION: Belorusskiy gosudarstvennyy universitet (Belorussian State University)

SUBMITTED: June 26, 1962 (initially)
October 22, 1962 (after revision)

Card 4/4

ACCESSION NR: AP4040373

S/0185/64/009/004/0349/0354

AUTHOR: Komarov, L. I.; Fisher, I. Z.

TITLE: Neutron and Optical Spectra as Sources of Information on the Motion of Molecules in Liquids /Paper presented at the Shestoye Soveshchaniye po Fizike Zhidkogo Sostoyaniya Veshchestva, Sixth Conference on the Physics of the Liquid State of Matter, Kiev, 1963/

SOURCE: Ukrayins'ky*y fizy*chny*y zhurnal, v. 9, no. 4, 1964, 349-354

TOPIC TAGS: liquid state, liquid state physics, liquid molecular motion, molecular radial density distribution, molecular correlation function, many-body problem, Van Hove time molecular distribution function, Rayleigh scattering, neutron scattering, fluctuation theory

TRANSLATION: The Van Hove time molecular distribution formalism is introduced and applied to the description of such kinetic properties of condensed phases as correlation and autocorrelation functions and fluctuations. The possibilities of obtaining information about these functions from experimental data are studied

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ACCESSION NR: AP4040373

in detail. It is shown that the Rayleigh scattering spectrum can be used to determine the asymptotic behavior of the Van Hove functions with respect to distance and time. Low energy neutron scattering by liquids is considered in detail with a view toward extracting information about nolecular distributions. The high frequency limit of sound propagation in liquids is considered, and the possibility of the existence of transverse waves in liquids is likewise treated. The phonon approach of solid state usage is modified to treat the neutron scattering problem in liquids. Though neutron scattering differential cross-sections and the angular distribution of Rayleigh scattering are not expected to be precisely conformal, they are expected to be closely related. Very low energy neutron scattering is recommended as a tool for studying the nature of molecular behavior which gives rise to the dispersion of elastic and kinetic coefficients in liquids at the high frequency limit. Orig. art. has 17 numbered equations.

ASSOCIATION: Belorusskiy Gosuniversitet, Minsk (Byelorussian State University)

SUBMITTED: 00 DATE ACQ: 13May64 ENCL: 00

SUB CODE: OP,GP NO REF SOV: 006 OTHER: 001

Card 2/2

ACCESSION NR: AP4040375 S/0185/64/009/004/0379/0383

AUTHOR: Fisher, I. Z.

TITLE: On the Theory of Diffusion Near the Critical Point [Paper presented at the Shestoye Soveshchaniye po Fizike Zhidkogo Sostoyaniya Veshchestva, Sixth Conference on the Physics of the Liquid State of Matter, Kiev, 1963.]

SOURCE: Ukrayins'ky*y fizy*chny*y zhurnal, v. 9, no. 4, 1964, 379-383

TOPIC TAGS: Thermodynamics, diffusion, liquid diffusion, critical point, diffusion coefficient, critical point diffusion, Onsager kinetic coefficient, Brownian motion, liquid kinetics, entropy

TRANSLATION: A treatment, more exact than those extant, is presented for the theory of diffusion processes in a binary-system near the critical point. The diffusion coefficient of any component is proportional to the partial derivative of its chemical potential with respect to its concentration:

$$D(c) \sim \left(\frac{\partial \mu}{\partial c}\right)_T . \qquad (1)$$

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ACCESSION NR: AP4040375

At the critical point, however

$$D(c) \sim \left(\frac{\partial \mu}{\partial c}\right)_T = 0 .$$

Thus, diffusion should cease at the critical point. Any supposition based on the absence of molecular mixing, even for a single state of a substance, would contradict a molecular-kinetic approach. This difficulty justifies the investigation, which is based on the deviation of the entropy from its equilibrium value. The expression for entropy contains as one of its terms the gradient of the off-equilibrium concentration deviation, δc. Differential equations are obtained for "critical diffusion", and Green's functions of these equations are constructed for one- and three-dimensional cases. If δc is treated as a "phase", its "center of gravity" changes with a characteristic time

$$\langle |x| \rangle = \text{const} \sqrt[4]{4Ht} \qquad (21)$$

according to the present treatment for the critical point. The usual diffusion theory analogue is

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$$\langle |x| \rangle = \text{const}\ \sqrt{2Dt}\ , \qquad (22)$$

where t is the time and D H. Thus, the slow nature — slow, yet still non-zero — of the diffusion is explained by the small value of H as well as the $t^{\frac{1}{4}}$ dependence. Also in contrast to the usual diffusion theory, a fundamental difference is seen to exist between macroscopic diffusion and Brownian motion of individual particles: the Green's functions have negative values at particulat transition probabilities for Brownian particles. Orig. art. has: 35 formulas.

ASSOCIATION: Belorusskiy Gosuniversitet, Minsk (Byelorussian State University)

SUBMITTED: 00 DATE ACQ: 13May64 ENCL: 00

SUB CODE: GP NO REF SOV: 003 OTHER: 000

Card 3/3

FISHER, I.Z.; SOSHINA, N.V.; ZAYTSEVA, A.M.

Density microfluctuations in simple liquids. Ukr. fiz. zhur. 9 no.5: 476-480 My '64. (MIRA 17:9)

1. Belorusskiy gosudarstvennyy universitet, Minsk.

FISHER, I.Z.

Comments on the kinetic theory of liquids. Zhur. fiz. khim. 38 no.3:778-780 Mr '64. (MIRA 17:7)

1. Belorusskiy gosudarstvennyy universitet.

FISHER, I.Z.; ZAYTSEVA, A.M.

Effect of the hydration of ions on the volume viscosity of electrolyte solutions. Dokl. AN SSSR 154 no.5:1175-1178 F'64.

1. Belorusskiy gosudarstvennyy universitet im. V.I.Lenina. Predstavleno akademikom I.I. Chernyayevym.

KOMAROV, L.I.; FISHER, I.Z.

Neutron and optical spectra as sources of information on the motion of molecules in liquids. Ukr. fiz. zhur. 9 no.4:349-354 Ap '64. (MIRA 17:8)

1. Belorusskiy gosudarstvennyy universitet, Minsk.

FISHER, I.Z.

Theory of diffusion near the critical point. Ukr. fiz. zhur. 9 no.4:379-383 Ap '64. (MIRA 17:8)

1. Belorusskiy gosudarstvennyy universitet, Minsk.

ZAYTSEVA, A.M.; FISHER, I.Z.

Hydration theory. Ukr. fiz. zhur. 9 no.4:383-387 Ap '64. (MIRA 17:8)

1. Belorusskiy gosudarstvennyy universitet, Minsk.

FISHER, I.Z.

Laminar nature of a diffusion flow near the critical point in a binary solution. Dokl. AN SSSR 158 no.5:1075-1077 O '64.

(MIRA 17:10)

1. Odesskiy gosudarstvennyy universitet im. I.I.Mechnikova. Predstavleno akademikom M.A.Leontovichem.

FISHER, I.Z.; KOVALENKO, N.P.

Effect of walls on the fluctuation level near the critical point.
Zhur.fiz.khim. 39 no.10:2569-2571 O '65.

(MIRA 18:12)

1. Odesskiy gosudarstvennyy universitet imeni Mechnikova.
Submitted June 6, 1964.

FISHER, I.Z.; YUL'MET'YEV, R.M.

Use of an electronic computer in studying thermal motion in a fluid. Usp. fiz. nauk 87 no.2:374-378 O '65.
(MIRA 18:11)

FISHER, K,

FISHER, K.; SKARICA, R. Electric transmission linesiin Croatia. p. 249

Vol. 9, no. 4/5, Apr./May 1956
ELEKTROPRIVERDA
TECHNOLOGY
Beograd

So: East European Accession, Vol. 6, no.3, March, 1957

BABENKO, P.; FISHER, L.; SAMARIN, A.; RUDENKO, P.

This is most important in educational work. Sov. profsoiuzy 17 no.18:21 S '61. (MIRA 14:8)
(Community centers)
(Trade unions)

DEKHTYAR, B.; FISHER, L. ; UDATOV, A. (g.Mogocha, Chitinskoy obl.);
TOLETIY, P. (g. Yagotin, Kiyevskaya obl.); SOLODOVNIKOV, I.
(Primorskiy kray); MUN'KO.T. (g. Zaporozh'ye)

Letters and correspondence. Sov.profsoiuzy 17 no.22:42-44 N
'61. (MIRA 14:10)

1. Spetsial'nyy korrespondent zhurnala "Sovetskiye profsoyuzy".
(Community centers, Mobile)
(Ural Mountain region—Callisthenics)
(Adult education)

NAZARENKO, P. (Astrakhanskaya oblast'); KIL'DIBEKOV, V. (g.Slobodskoy, Kirovskaya oblast'); DEVYATOVSKIY, M. (g.Orsk); SERGIYENYA, K. (g.Khar'kov); FISHER, L.; BELYAYEV, A.; VENGEROV, A.; KRAVTSOV, S. (g.Khar'kov)

Readers relate, advise and criticise. Sov. profsoiuzy 18 no.15:26-28 Ag '62. (MIRA 15:7)

1. Neshtatnyy korrespondent zhurnala "Sovetskiye profsoyuzy" (for Nazarenko, Sergiyenya, Vengerov). 2. Sotrudnik gorodskoy gazety "Leninskiy put'" (for Kil'dibekov). 3. Sotrudnik neshtatnogo otdela oblostnogo kimiteta profsoyuza rabochikh metallurgicheskoy promyshelnnosti (for Devyatovskiy). 4. Predsedatel' komiteta profsoyuza elektromekhanicheskogo zavoda, g.Khar'kov (for Kravtsov).
(Socialist competition) (Ust'-Kamenogorsk--Housing)
(Kharkov--Electric equipment industry)

FISHER, L. (Krasnaya Polyana, Moskovskaya obl.)

Our IUrii Gagarin. Sov. profsoiuzy 18 no.7:9 Ap '62.
(MIRA 15:3)

1. Spetsial'nyy korrespondent zhurnala "Sovetskiye profsoyuzy".
(Krasnaya Polyana—Cotton spinning) (Socialist competition)

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

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Ca

Hess's synthesis of arecaidine and arecoline. N. A. Preobrazhenskii and L. B. Fisher. *J. Gen. Chem.* (U. S. S. R.) 11, 140-2(1941).—Arecoline, a valuable pharmaceutical, was reported to have been synthesized by a simple method from nicotinic acid by Hess and Leibbrandt (*C. A.* 13, 580). In trying to improve the procedure of H. and L., the authors found that the method does not yield the desired product and that the data given by H. and L. apply to an intermediate in their synthesis and not to arecoline. Nicotinic acid-HCl was hydrogenated in 25% H_2O soln. with a Pt catalyst at 1.5 atm. pressure to yield 70% of *hexahydronicotinic acid-HCl* (I), m. 233-4° (from EtOH). Treatment of I with an equal amt. of 35% formalin and 0.75 part of H_2O, heating till soln. occurred, followed by 2 mols. of HCO_2H and heating on a steam-bath for 15 hrs., and distn. of the H_2O *in vacuo* gave 90% of *N-methylhexahydronicotinic acid* (II), m. 176-8°. Soln. of II in 5 times its wt. of MeOH satd. with HCl and boiling for 24 hrs. yielded, on evapn. of H_2O *in vacuo* followed by neutralization by soda, 66% of the *Me ester* (III), b_{14-15} 80-2°. III.HBr m. 115-16°; III.MeI m. 194-5°. III (5.2 g.) in 20 cc. MeOH, treated with 5.2 g. Br in 15 cc. MeOH, refluxed for 2 hrs., cooled, treated with MeONa (from 1.4 g. Na), refluxed 0.5 hr., MeOH added, satd. with HCl, and refluxed for 24 hrs., yields, upon neutralization by soda and Et_2O extn., a base, b_{14} 74-6°. H. and L. give b_{17} 94°. The product gives an HCl salt and methiodide identical with those of III. Heating of III with Br in $CHCl_3$ in a sealed tube at 100° yielded II.HBr, m. 193-5°. Hess considered this to be arecaidine-HBr. However, 0.5 g. natural arecoline refluxed for 10 hrs. with 1 cc. 48% HBr in 50 cc. H_2O yields authentic arecaidine-HBr, white, m. 242-3°, entirely different from H. and L.'s supposed synthetic product.

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

BC

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

MATERIALS INDEX

AUTHOR INDEX

1ST AND 2ND ORDERS

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C4

Derivatives of C_4H_4. XL. Hydrogenation of secondary vinylethynylcarbinols. I. N. Nazarov and L. B. Fisher. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* **1944**, 341-8 (English summary); cf. *C.A.* **39**, 1619[a]. It was shown that secondary vinylethynyl alcs. [methyl(vinylethynyl)carbinol (I), ethyl(vinylethynyl)carbinol (II), and propyl(vinylethynyl)carbinol (III)] hydrogenate readily on shaking with Cu-Zn dust in water, with smooth formation of the corresponding 1,3-diene alcs. The increase of the radical size in this series does not affect the rate or direction of the hydrogenation reaction. Thus 25 g. I, 50 cc. Et_2O, 30 g. coppered Zn dust, and 20 cc. H_2O shaken for 150 hrs. gave 18 g. *1,3-hexadien-5-ol*, b_{14} 44-5°, n_D^{20} 1.4772, d_4^{20} 0.8727, which hydrogenates readily with H in contact with Pd on $CaCO_3$ to yield BuCH(OH)Me, which can be obtained by similar hydrogenation of the original I. II treated with Cu-Zn as above gave *1,3-heptadien-5-ol*, b_{16} 59-60°, n_D^{20} 1.4880, d_4^{20} 0.8718, which readily hydrogenates over Pd to BuCH(OH)Et. III treated with Cu-Zn as above gave *1,3-octadien-5-ol*, b_{16} 74°, n_D^{20} 1.4785, d_4^{20} 0.8643, which was readily hydrogenated in the presence of Pd to BuCH(OH)Pr. The catalytic hydrogenation (over Pd) rate of the secondary ethynyl alcs. does not differ materially from that of tert. alcs.; after addn. of 2H there was no noticeable change in the reaction rate, although an appreciable rate drop occurs after addn. of 4H. G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Derivatives of acetylene. XLII. Rearrangement of the 1,3-diene system. Reversible isomerization of 1,3-diene alcohols with migration of the hydroxyl to the δ-position. I. N. Nazarov and I. B. Fisher (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1948, 631-7(in English, 638); cf. *C.A.* 40, 2781[1].—When $Me_2C(OH)CH{:}CHCH{:}CH_2$ (I), b_{10} 44-5°, is shaken with 3 times its vol. of 3% H_2SO_4 at room temp. for 9-10 hrs. it forms an equil. mixt. with its isomer, *5-methyl-2,4-hexadien-1-ol* (II), b_6 75-6°, n_D^{20} 1.5060, d_4^{20} 0.8917, *MR* calcd. 35.2, found 37.3. The reaction product contains 60-80% of a mixt. of I and II and 20-40% higher-boiling condensation and polymerization products. If higher acid concns. are used, more polymerization occurs. II is partly converted to I under the same conditions. $KMnO_4$ oxidation of II gives Me_2CO and $(CO_2H)_2$. Hydrogenation of II over Pt gives isoheptyl alc. When II is hydrogenated over Pd, it absorbs only 1 mol. H to give a mixt. of all 3 possible isomeric olefins. Hydrogenation of this mixt. over Pt gives the satd. alc. I hydrogenates over Ni or Pd to give a mixt. of only 2 olefins, and, on longer reaction over Pd or rapidly over Pt, it forms Me_2BuCOH. H. M. Leicester

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Acetylene derivatives. LX. Reversible rearrangements of the 1,3-diene system in exchange reactions. Chlorides of 1,3-diene alcohols. I. N. Nazarov and L. B. Fisher. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1948, 311-15; cf. *C.A.* 42, 7730c.—5-Methyl-1,3-hexadien-5-ol was prepd. by reduction of $Me_2C(OH)$-$CH:CHC:CH$ by means of Cu-Zn dust and H_2O, and the product, isomerized by 3% H_2SO_4, gave *5-methyl-2,4-hexadien-1-ol* (I), b_9 76-8°, n_D^{20} 1.5060. I (22.5 g.) in 40 ml. dry Et_2O was satd. in 1 hr. with dry HCl (7.5 g.) at −8° and let stand at room temp. 1.5-2 hrs.; the org. layer, sepd. and washed with Na_2CO_3, then water, gave on distn. 60-2% *5-methyl-1-chloro-2,4-hexadiene*, b_{11} 57-8°, n_D^{20} 1.5120, d_4^{20} 0.9410, colorless liquid with a sharp odor, clouds and yellows rapidly on standing; its Cl is quantitatively removed by $AgNO_3$ in alc. in 3 hrs. at 65-70°. The chloride (10.5 g.) stirred with 8 g. $NaHCO_3$ in 50 ml. H_2O 1 hr. at room temp. and 4 hrs. at 50-5° gave 6 g. *5-methyl-1,3-hexadien-5-ol* (II), b_9 44-5°, n_D^{20} 1.4760, d_4^{20} 0.8580, which on reduction with H in EtOH in the presence of Pt gave $Me_2C(OH)Bu$, b. 137-8°. The chloride on oxidation with aq. $KMnO_4$ in the cold gave Me_2CO, $(CO_2H)_2$, HCO_2H, and $Me_2C(OH)CO_2H$, b_9 108-11°, m. 77-8° (from benzene); oxidation in Me_2CO soln. gave the same result. Ozonization of the chloride gave a little Me_2CO peroxide, HCO_2H, and $Me_2C(OH)CO_2H$. Addn. of 18 g. of the chloride to 16 g. KOAc in 40 ml. AcOH in 0.5 hr., stirring 3 hrs. at 45-50°, and letting stand overnight gave: (1) a mixt. of II and its *acetate*, b_9 44-5°, (2) 7 g. I *acetate*, b_9 85-6°, n_D^{20} 1.4830, d_4^{20} 0.9298, and (3) 1.2 g. crude acetate-II mixt., b_9 45-85°. I acetate (6.16 g.) added to 2.4 g. KOH in 40 ml. EtOH, let stand overnight, heated 1 hr. to 55-60°, carefully neutralized with 2% AcOH, and distd. gave 4 g. I, hydrogenated in Et_2O over Pt to isoheptyl alc., b. 167-9°. II (25 g.) in 30 ml. Et_2O treated with 8.5 g. dry HCl at −8°, and the sepd. org. layer rapidly washed after 2 hrs. and distd. yielded 17 g. 1-chloro-5-methyl-2,4-hexadiene, identical with the above described sample, as well as 3 g. of a lower-boiling fraction, b_{11} 42-50°, n_D^{20} 1.4930, which may contain some 5-chloro-5-methyl-1,3-hexadiene. The acetylation of the chloride with KOAc-AcOH, thus, leads predominantly to the unisomerized acetate of I (about 80%), and to some 20% of the isomerized product (II) and its acetate; these were not sepd. into pure compds. **LXI. Rearrangements of 1,3-diene systems. 3. Reversible isomerization of 1,3-hexadien-5-ol into 2,4-hexadien-1-ol (sorbic alcohol) and the rearrangement of the corresponding chlorides in an exchange reaction.** *Ibid.* 427-35.—$MeCH(OH)C:CCH:CH_2$ (110 g.), 200 ml. Et_2O, 49 g. Cu-Zn dust, and 30 ml. H_2O were stirred 10 hrs. at room temp. and 10 hrs. at 35-40°, then treated with 40 g. Cu-Zn dust and 30 ml. H_2O and stirred as above; in all, 4 such addns. were performed during a total period of 90 hrs.; the usual treatment gave 100 g. *1,3-hexadien-5-ol* (I), b_{15} 54-5°, n_D^{20} 1.4790.

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19 g. crude V. Pure IV, b. 106-10°, n_D^{20} 1.4130, d_4^{20} 0.8010, on hydrogenation in Et_2O over Pd gave *methylethylcarbinol Me ether*, b. 111-12°, n_D^{20} 1.4055, d_4^{20} 0.7977, while oxidation with $KMnO_4$ gave HCO_2H and methylethylmethoxyacetic acid, b_{20} 110-13°, n_D^{20} 1.4230. Pure V, b. 127-9°, n_D^{20} 1.4235, d_4^{20} 0.8103, on hydrogenation in Et_2O over Pd gave *1-methoxy-3-methylpentane*, b. 118-19°, n_D^{20} 1.4030, d_4^{20} 0.7834, while oxidation with $KMnO_4$ gave MeEtCO and $MeOCH_2CO_2H$. Heating 28 g. III and 68 ml. 3% H_2SO_4 in MeOH 10 hrs. at 60-5°, followed by diln. with 116 ml. H_2O, and washing the org. layer with H_2O and 1% aq. Na_2CO_3, gave 11.2 g. III and 3.6 g. II, while a small amt. of isoprene was also found. Heating 10 g. IV and 20 ml. 3% H_2SO_4 in MeOH 10 hrs. at 60-5° gave 1.2 g. IV and 1.3 g. V, as well as 2.1 g. intermediate fraction and 0.9 g. crude 3-methyl-1,3-pentadiene. The ether isomerization probably does not occur by migration of the MeO group, but with formation of an intermediate sulfate ester which displaces the MeO group. LXIII.

Reversible rearrangements of allylic systems. Action of hydrogen chloride on 1,1- and 3,3-dimethylallylcarbinols and isomeric transformations of 1,1- and 3,3-dimethylallyl chlorides in exchange reactions. I. N. Nazarov and I. N. Azerbaev. *Ibid.* 414-23.—Action of HCl on tertiary 1,1-dialkylallyl alcs. leads to chlorides of predominantly primary structure, while hydrolysis of the chlorides gives a reverse rearrangement with formation of the original tertiary alcs. The isomer ratio obtained in rearrangements of allylic or 1,3-diene systems depends on the structure of the starting materials (degree of substitution, pos. charge distribution, and isomerization rate) and on the nature of the anion which dets. the ease of its cleavage and formation of carbonium ions. $Me_2C(OH)CH:CH_2$, b. 95-7°, n_D^{20} 1.4140, (180 g.) treated with ice cooling with 78 g. dry HCl over 5 hrs., at room temp., and the aq. layer sepd. after 2 hrs. and the org. layer washed with cold 10% $NaHCO_3$, yielded 188 g. crude chlorides, fractionated into 44 g. *1,1-dimethylallyl chloride* (I), b_{100} 42-5°, n_D^{20} 1.4190, and 140 g. *3,3-dimethylallyl chloride* (II), b_{100} 61-3°, n_D^{20} 1.4485. The carbinol (100 g.) with 53 g. dry HCl at −15° similarly gave 27.5 g. I and 51.6 g. II, with 20.4 g. intermediate fraction; the result was the same when the reaction was run at −35°. $Me_2C:CHCH_2OH$ (21.5 g.) treated at 0° with 9.1 g. dry HCl gave 1 g. I and 14 g. II. Pure I b_{100} 42-5°, b. 83-6° (some decompn.), n_D^{20} 1.4190, d_4^{20} 0.8795; standing 3 months in a sealed tube led to isomerization, giving 1.0 g. I and 0.8 g. II; hydrolysis of 2 g. I with 30 ml. 10% aq. $NaHCO_3$ 1 hr. at room temp. and 5 hrs. at 43° gave 1.5 g. $Me_2C(OH)CH:CH_2$; 10 g. I and 5 g. Na in 50 ml. MeOH after 1 hr. at room temp. and 6 hrs. at 60° gave 4 g. $Me_2C(OH)CH:CH_2$ (see preceding abstr.) and 2 g. $Me_2C(OMe)CH:CH_2$; stirring 15 g. I and 16 g. KOAc in 60 ml. AcOH 2 hrs. at room temp. and 8 hrs. at 50-60°, followed

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by standing overnight, filtration, and washing in Et_2O soln. with H_2O and 5% $NaHCO_3$, gave 3.6 g. *dimethylvinylcarbinyl acetate*, b. 120-2°, n_D^{20} 1.4120, and 3.1 g. *3,3-dimethylallyl acetate*, b. 149-51°, n_D^{20} 1.4281. Pure II b_{100} 61-3°, n_D^{20} 1.4485, d_4^{20} 0.9273 which does not change on 5-month storage nor on heating 10 hrs. at 60°. $AgNO_3$ in aq. alc. immediately removes Cl from I and II. Ozonization of II in $CHCl_3$ gave acetone *peroxide*, m. 131-2°, HCO_2H, and $ClCH_2CO_2H$. Hydrolysis of 8 g. II with 80 ml. 10% $NaHCO_3$ 1 hr. at room temp., then 4 hrs. at 50°, gave 4 g. $Me_2C(OH)CH:CH_2$ and 0.9 g. $Me_2C:CHCH_2OH$. II (21.6 g.) added slowly to 7 g. Na in 100 ml. MeOH, let stand overnight, and heated 6 hrs. to 60°, gave 16.5 g. $Me_2C:CHCH_2OMe$; a similar reaction using a crude chloride mixt. from 48 g. carbinol gave 5 and 33 g., resp., of the isomeric ethers. II (15 g.) with 8 g. Na in 100 ml. PrOH gave 8 g. *3,3-dimethylallyl Pr ether*, b. 144-5°, n_D^{20} 1.4214, d_4^{20} 0.7999; iso-PrOH similarly gives the corresponding *iso-Pr ether*, b. 129-30°, n_D^{20} 1.4190, d_4^{20} 0.8020; BuOH gave the *Bu ether*, b. 165-7°, n_D^{20} 1.4260, d_4^{20} 0.8047; iso-BuOH gave the *iso-Bu ether*, b. 157-9°, n_D^{20} 1.4230, d_4^{20} 0.7977. Stirring 33 g. II and 42 g. KOAc in 120 ml. AcOH 2 hrs. at room temp. and 8 hrs. at 50-60° gave 96% KCl and the org. layer, after washing, yielded 7 g. $Me_2C(OAc)CH:CH_2$, b. 120-2°, n_D^{20} 1.4121, d_4^{20} 0.8940, (on hydrolysis with 10% KOH this gave $Me_2C(OH)CH:CH_2$), and 15 g. $Me_2C:CHCH_2OAc$, b. 149-51°, n_D^{20} 1.4283, d_4^{20} 0.9169 (on hydrolysis with 10% KOH this gives $Me_2C:CHCH_2OH$). Similar treatment of 49 g. crude chloride mixt. gave 12 g. of the former and 25 g. of the latter acetate, which is explained by the compensation of isomerization of the primary chloride by reverse isomerization of the tertiary chloride. **LXIV. Rearrangements of the allylic system. 4. Action of hydrogen chloride on methylpropylvinylcarbinol and 3-methyl-3-propylallyl alcohol and isomerization of the corresponding chlorides in exchange reactions.** I. N. Nazarov, I. N. Azerbaev, and V. N. Rakcheeva. *Ibid.* 650-64.—The greater mobility of a dialkyl system in comparison with the monoalkyl system demonstrates the inductive effect of the alkyl groups, which influences the rearrangements in the 1,3-dienes. *$MePr(HO)CCH:CH_2$* (I), b. 134-6°, n_D^{20} 1.4305, was prepd. according to N., *et al.* (*Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1946, 305). I (142 g.) treated with ice cooling with 47 g. dry HCl in 4 hrs. and let stand 2 hrs. gave, after rapid washing, 20 g. *$MePrCClCH:CH_2$* (II), b_{50} 40-50°, n_D^{20} 1.4345, d_4^{20} 0.8708, and 85 g. *$MePrC:CHCH_2Cl$* (III), b_{20} 60-1°, n_D^{20} 1.4535, d_4^{20} 0.9106.

Ozonization of II gave HCO_2H, $MePrC(OH)CO_2H$, and a little corresponding Cl acid. On standing 2 months II yellowed, its n increased, and it yielded 0.8 g. III. Stirring 5 g. II and 40 ml. 10% $NaHCO_3$ 1 hr. at room temp. and 3 hrs. at 45-50° gave only I; 10% KOH gave the same result; only a trace of the isomeric alc. might have been present in the final drops of the distillates. II (10 g.) added slowly with cooling to 2 g. Na in 50 ml. MeOH, let stand overnight, and heated 6 hrs. to 50-60°, gave 4 g. NaCl and 4.5 g. crude *$MePrC:CHCH_2OMe$*, b. 130-48°, n_D^{20} 1.4240; approx. 25% of the isomeric *$MePrC(OMe)CH:CH_2$* was formed but could not be obtained in a pure state because of the small amts. used. II (10 g.), 9 g. KOAc, and 40 ml. AcOH stirred 2 hrs. at room temp. and 8 hrs. at 50-60° gave 5.3 g. KCl; the filtrate, neutralized with 40% KOH in the cold, extd. with Et_2O, the ext. evapd., mixed with 50 ml. 10% KOH-MeOH, let stand overnight, heated 3 hrs. to 60-70°, concd., dild. with H_2O, extd. with Et_2O, and distd. yielded 2 g. I and 2 g. *$MePrC:CHCH_2OH$* (IV), b. 170-2°, b_{44} 90-100°, n_D^{20} 1.4450. The acetates were hydrolyzed because they are better separable in the form of alcs. III on standing 3 months remains colorless but loses some HCl and its n is unchanged; its ozonization gives no HCO_2H, and the products include $ClCH_2CO_2H$ and MePrCO; hydrolysis of

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sulfate stirred 2 hrs. at 60°, then treated in 2 portions with 10 g. Hg sulfate with a 2-hr. interval, stirred 6 hrs. at 60°, and worked up as above, gave 212 g. products, predominantly the above *MeO ketone* (VI), b_{11} 98°, n_D^{20} 1.4640, d_4^{20} 0.9243. V (7.8 g., fraction b_{11} 80–2°) in 20 ml. EtOH hydrogenated over Pt oxide gave 6 g. *5-methyl-4-octanone*, b_{20} 67–8°, b. 174–6°, n_D^{20} 1.4207, d_4^{20} 0.8227, which failed to give a cryst. oxime or semicarbazone. Ozonization of V gave HCO_2H, AcOH, and $EtCO_2H$. V (5 g.) and 10 g. H_3PO_4 (d. 1.78) stirred 2 hrs. at 60° gave 3 g. of previously described *1,3-dimethyl-2-ethyl-1-cyclopenten-5-one* (VII), b_{11} 89–91°, n_D^{20} 1.4838; [*semicarbazone*, m. 186–7° (from alc.); *2,4-dinitrophenylhydrazone*, m. 165° (from alc.)]; similar results were obtained by cyclization with HCl at 60–5° or with p-$MeC_6H_4SO_3H$ at 120–30°. VI (9 g.) and 0.05 g. p-$MeC_6H_4SO_3H$ heated on steam bath at 95 mm. 1.25 hrs. gave 7 g. *high-boiling isomer of 5-methyl-1,5-octadien-4-one*, b_9 80–3°, n_D^{20} 1.4800, d_4^{20} 0.9057, which on hydrogenation gave the same results as the low-boiling isomer described above. III (60 g.) and 120 g. H_3PO_4 (d. 1.78) were stirred 5 hrs. at 65°, yielding 20 g. starting material and 30 g. VII, b_{14} 92–3°, d_4^{20} 0.9330; the same product was obtained when concd. H_2SO_4 was used under the same conditions. VII (12.8 g.) in 40 g. AcOH was hydrogenated over Pt oxide, yielding *1,3-dimethyl-2-ethyl-5-cyclopentanone*, b_{14} 72–5°, b. 180–3°, n_D^{20} 1.4470, d_4^{20} 0.8942; *semicarbazone*, m. 181–2° (from EtOH). IV (53 g.) in 123 g. 85% MeOH, treated with 0.7 ml. H_2SO_4 and 2 g. Hg sulfate and stirred 1 hr. at 65°, then treated with a 2-hr. interval with 2 g. Hg sulfate in 2 portions and stirred 6 hrs. at 65°, gave, after the above-described treatment, 53 g. *5-ethyl-1,5-heptadien-4-one*, b_{20} 75–80°, n_D^{20} 1.4770, which on fractionation appeared to exist in 2 isomeric forms, of which the *higher-boiling form* (VIII) only was studied; it b_{14} 78–80°, n_D^{20} 1.4800, d_4^{20} 0.9035, polymerizes slowly on standing; ozonization gave HCO_2H, AcOH, and $EtCO_2H$. VIII (7 g.) and 30 ml. HCl stirred 3 hrs. at 60–5° gave 5.5 g. *2,3-dimethyl-1-ethyl-1-cyclopenten-5-one* (IX), b_4 75–7°, n_D^{20} 1.4790; *semicarbazone*, m. 186–8° (from EtOH); the same product (b_4 75–6°, b_{12} 91–3°, n_D^{20} 1.4800, d_4^{20} 0.9262) was obtained when H_3PO_4 (d. 1.78) was used under similar conditions (the semicarbazone, here, m. 159–60°); hydrogenation in AcOH over Pt oxide gave *2,3-dimethyl-1-ethyl-5-cyclopentanone*, b_7 60–1°, n_D^{20} 1.4425; *semicarbazone*, m. 156–7° (from EtOH); ozonization of the cyclopentenone gave HCO_2H and $EtCO_2H$, and a little methyllevulinic acid (isolated as the semicarbazone, m. 172°). IV (15 g.) and 30 g. H_3PO_4 (d. 1.78) stirred 7 hrs. at 60–5° gave 10 g. IX (b_{12} 91–3°, n_D^{20} 1.4795, d_4^{20} 0.9257). IV (100 g.) and 500 ml. concd. HCl stirred 7 hrs. at 60–5° gave 28 g. of a mixt. of IX and an unknown cyclic ketone, b_{20} 90–7°, which gave 2 semicarbazones: the 1st, m. 170° (ppts. immediately), apparently is that of an isomer of IX, and the 2nd, m. 159–60° (isolated from the mother liquor), is that of the IX isomer obtained in the above expts.; in addn., the reaction products also yielded 10 g. of the other isomer of IX, b_{14} 98–9°, n_D^{20} 1.4860; *semicarbazone*, m. 190–1° (from EtOH). VIII (6 g.) treated with cooling with 6 g. H_3PO_4 (d. 1.78) and stirred 8 hrs. at 10–15° yielded 2.3 g. crude *2,3-dimethyl-1-ethylcyclopentan-3-ol-5-one*, b_{20} 108–10°, n_D^{20} 1.4660, d_4^{20} 0.9622; *semicarbazone*, m. 166–7° (from EtOH). LXVI. Mechanism of hydration and cyclization of dienynes. II. Hydration and cyclization of 4-methyl-1-vinylethynyl-cyclohexene. I. N. Nazarov and L. N. Pinkina. *Ibid.* 675–80; cf. *C.A.* 42, 7731i.—*4-Methyl-1-vinylethynylcyclohexenol*, prepd. as described earlier (*loc. cit.*) in 93% yield from $CH_2:CHC:CH$ and 4-methyl-cyclohexanone in the presence of powd. KOH, b_{4-5} 99–100°, n_D^{20} 1.5045. This (203 g.) and 200 ml. 50% H_2SO_4 stirred 1 hr. at 40° and 4 hrs. at 55–60° gave 160 g. *4-methyl-1-vinylethynylcyclohexene* (I), b_7 78–80°, n_D^{20} 1.5345 (88%). This (18 g.) and 18 ml. H_3PO_4 (d. 1.76) stirred 30 min. at room temp. and 6 hrs. at 60–5° gave 15.8 g. *1,6-dimethyl-4,5,6,7-tetrahydro-3-indanone* (II), b_{12} 125°, n_D^{20} 1.5050, d_4^{20} 0.9858; *semicarbazone*, m. 212° (from MeOH). This (4.8 g.) hydrogenated in MeOH with Raney Ni gave *1,6-dimethylhexahydro-3-indanone*,

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b_7 95-7°, n^{20}_D 1.4787, d^{20}_4 0.9581; *semicarbazone*, m. 184-5° (from MeOH; sealed capillary); in addn. there was obtained a small amt. of *1,6-dimethylhexahydro-3-indanol*, b_7 99°, n^{20}_D 1.4852, d^{20}_4 0.9634. I (60 g.), 170 ml. 85% MeOH, 1 g. H_2SO_4 (d. 1.83), and 3 g. Hg sulfate stirred 3 hrs. at 60° with addn. of 2 portions of 1.5 g. Hg sulfate at 1-hr. intervals gave, after filtration, removal of MeOH, extn. with Et_2O, and washing with soda soln., 63 g. mixed *allyl 4-methylcyclohexenyl ketone* and the *corresponding MeO ketone*, 4-$MeC_6H_8COCH_2CH(OMe)Me$, from which it was possible to isolate the latter in pure state, $b_{4.5}$ 118-19°, n^{20}_D 1.4804, d^{20}_4 0.9737. The above mixt. (54 g.) distd. in the presence of 0.3 g. *p*-$MeC_6H_4SO_3H$ at a water-pump vacuum yielded 40 g. *allyl 4-methylcyclohexenyl ketone*, $b_{4.5}$ 107-8°, n^{20}_D 1.5065, d^{20}_4 0.9583, which on hydrogenation in MeOH over Raney Ni gave *propyl 4-methylcyclohexyl ketone*, b_7 80-8°, n^{20}_D 1.4548, d^{20}_4 0.9018; *semicarbazone*, m. 134-5° (from MeOH). Ozonization of the unsatd. ketone gave HCO_2H and β-methyladipic acid, m. 91° (from benzene); traces of AcOH were detected. The unsatd. ketone (6 g.) and 6 ml. H_3PO_4 (d. 1.76) stirred 0.5 hr. at room temp. and 6 hrs. at 60-5° gave 4.4 g. II; the same resulted when concd. HCl was used. II (9.5 g.) and 9.5 ml. H_3PO_4 (d. 1.80) stirred 2 hrs. at 165-70° and 1.5 hr. at 100° gave 3.9 g. *1,6-dimethylindan*, $b_{4.5}$ 70-3°, b. 201°, n^{20}_D 1.5203, d^{20}_4 0.9301. **LXVII. Mechanism of hydration and cyclization of dienynes. 12. Hydration and cyclization of 5-methyl-1-vinylethynylcyclohexene.** *Ibid.* 681-5.—To 47 g. powd. KOH in 150 ml. dry Et_2O was added with cooling and stirring over 2 hrs. a mixt. of 75 g. 3-methylcyclohexanone and 45 g. $CH_2:CHC:CH$ in 100 ml. Et_2O; after stirring in the cold, with diln. with 50 ml. Et_2O, 3 hrs., letting stand overnight, and stirring 4 hrs., the mixt. was washed with water, and the Et_2O ext. washed with 8% HCl, giving 90 g. *1-vinylethynyl-5-methylcyclohexanol*, b_7 93-4°, n^{20}_D 1.5068, d^{20}_4 0.959. This (92 g.) and 80 ml. 50% H_2SO_4 stirred 2 hrs. at 40° and 3 hrs. at 60° gave 63 g. *1-vinylethynyl-5-methylcyclohexene*, b. 77-8° (pressure not stated), n^{20}_D 1.5332, d^{20}_4 0.8840. This (15 g.) and 15 ml. H_3PO_4 (d. 1.76), stirred 6 hrs. at 60-5°, gave 8.9 g. *1,5-dimethyl-4,5,6,7-tetrahydro-3-indanone*, b_7 108-9°, n^{20}_D 1.5055, d^{20}_4 0.9881; *semicarbazone*, m. 221° (from MeOH); this on hydrogenation gave (in MeOH over Raney Ni) in 8 days 0.7 g. *1,5-dimethylhexahydro-3-indanone*, b_7 94-6°, n^{20}_D 1.4758, d^{20}_4 0.9583; *semicarbazone*, m. 190-1° (from MeOH; sealed capillary). The cyclohexene (44 g.), 153 g. 90% MeOH, 1 g. H_2SO_4, and 2.5 g. Hg sulfate stirred 2.5 hrs. at 60-5°, with gradual addn. of 2 g. Hg sulfate, gave 47.4 g. *allyl 5-methylcyclohexenyl ketone* mixed with some *corresponding MeO ketone* (addn. to the vinyl group), b_7 104-14°; distn. of the mixt. in the presence of *p*-$MeC_6H_4SO_3H$ *in vacuo* gave 30.5 g. pure *allyl 5-methylcyclohexenyl ketone*, yellow, b_7 104-6°, n^{20}_D 1.5086, d^{20}_4 0.9564, which on hydrogenation in EtOH over Raney Ni gave *propyl 5-methylcyclohexenyl ketone*, b_7 85-7°, n^{20}_D 1.4538, d^{20}_4 0.9006; *semicarbazone*, m. 122.5-3° (from 50% EtOH). Ozonization of the allyl ketone gave HCO_2H and β-methyladipic acid; traces of AcOH were found. The allyl ketone (8 g.) and 8 ml. H_3PO_4 (d. 1.76) stirred 0.5 hr. at room temp. and 5.5 hrs.

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III by 10% $NaHCO_3$ gave 85% I and 15% IV, while treatment with MeONa in MeOH, as above, gave 100% *MePrC:CHCH₂OMe*, b. 148-9°, n_D^{20} 1.4280, d_4^{20} 0.8148, which on hydrogenation over Pt catalyst gave 1-methoxy-3-methylhexane, b. 143-4°, n_D^{20} 1.4172, d_4^{20} 0.8015; III treated with KOAc in AcOH, as above, gave 65% IV and 35% I. It was possible to isolate only small amts. of pure isomeric acetates by prolonged fractionation: I *acetate*, b_{14} 78-80°, n_D^{20} 1.4240; IV *acetate*, b_{14} 103-4°, n_D^{20} 1.4370. I (48 g.) added slowly to 40 g. Ac_2O contg. 2 drops H_2SO_4 with cooling, let stand overnight, washed, neutralized, and distd. after drying, gave 13 g. I *acetate* and 9 g. IV *acetate*, as well as 5 g. crude *3-methyl-1,3-hexadiene*, b. 90-101°, and 8 g. unidentified condensation products, b_{14} 85-120°. I acetate obtained here appeared to be the purest sample obtained, b_{14} 75-6°, n_D^{20} 1.4220, d_4^{20} 0.8949, and on hydrogenation over Pt catalyst gave *methylethylpropylcarbinyl acetate*, b_{14} 72-3°, n_D^{20} 1.4140, while its hydrolysis by 10% KOH in MeOH gave 100% I. IV acetate obtained by the Ac_2O reaction was also the purest sample obtained; it b_{14} 80-1°, n_D^{20} 1.4360, d_4^{20} 0.9037, and was hydrogenated to *3-methyl-1-hexanol acetate*, b_{14} 70-2°, n_D^{20} 1.4180, d_4^{20} 0.8735, and hydrolyzed by 10% KOH-MeOH to 100% IV. Passage of dry HCl into IV in the cold gave 97% III and 3% II. **LIV. Mechanism of hydration and cyclization of dienynes. 10. Hydration and cyclization of 5-methyl-1,5-octadien-3-yne and 5-ethyl-1,5-heptadien-3-yne.** I. N. Nazarov and I. I. Zaretskaya. *Ibid.* 665-74; cf. *C.A.* 42, 7731a.—To 600 g. powd. KOH in 800 ml. Et_2O were added with cooling 800 g. MePrCO and 640 g. $CH_2:CHC:CH$ in 800 ml. Et_2O; stirring 3 hrs. in the cold and 5 hrs. at room temp., washing, and neutralization gave 75% *PrMeC(OH)C:CCH:CH₂* (I), b_{14} 80°, n_D^{20} 1.4740. Similarly Et_2CO gave 82% *Et₂C(OH)C:CCH:CH₂* (II), b_{14} 83-4°, n_D^{20} 1.4800. I (330 g.) and 330 g. 50% H_2SO_4 stirred 5 hrs. at 60-5° gave 250 g. *5-methyl-1,5-octadien-3-yne* (III), b_{14} 49-50°, n_D^{20} 1.5020 (80%). Similar dehydration of II gave 84% *5-ethyl-1,5-heptadien-3-yne* (IV), b_{14} 53-5°, n_D^{20} 1.5020. III (195 g.), 600 g. 85% MeOH, 2 ml. H_2SO_4, and 5 g. Hg sulfate stirred 20 min. at 60-5°, then treated every 20 min. with addnl. Hg sulfate until the total amt. was 15 g., then stirred 1 hr. at 60-5°, and the mixt. freed of excess MeOH *in vacuo*, gave 161 g. dehydration products, b_{14} 45-100°, which on exhaustive fractionation gave 30 g. III, 22 g. of a mixt. of III and *Me(EtCH:)CCOCH₂CH:CH₂*, b_{14} 65-77°, n_D^{20} 1.4883-1.4800, 62 g. of a mixt. of isomeric *5-methyl-1,5-octadien-4-ones* (V), b_{14} 77-89°, and 39 g. of a mixt. of V with *Me(EtCH:)CCOCH₂CH(OMe)Me*, b_{14} 89-103°, n_D^{20} 1.4710-1.4630. Pure V fraction, b_{14} 80-2°, n_D^{20} 1.4750, d_4^{20} 0.8849, gave a *2,4-dinitrophenylhydrazone*, m. 156-7° (from alc.). III (188 g.), 880 g. 90% MeOH, 4.5 ml. H_2SO_4, and 6 g. Hg

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at 65° gave 5.8 g. *1,5-dimethyl-4,5,6,7-tetrahydro-3-indanone*, b_1 109-10°, n_D^{20} 1.5050 [*semicarbazone*, m. 221° (from MeOH)], identical with the above described. This (10 g.) and 10 ml. H_3PO_4 (d. 1.80) stirred 2 hrs. at 165-70° and 1.5 hrs. at 190-5° gave 3.2 g. *1,5-dimethylindan*, b_{10} 75-6°, n_D^{20} 1.5210, d_4^{20} 0.9325. LXVIII. Mechanism of hydration and cyclization of dienynes. 13. Hydration and cyclization? of 2-*tert*-butyl-1,5-hexadien-3-yne. I. N. Nazarov and I. L. Kotlyarevskii. *Ibid.* 896-902 (1948); cf. N. and Zaretskaya, *C.A.* 37, 6243[1].—Me_3CAc (210 g.), 140 g. $CH_2:CHC:CH$, and 300 ml. dry Et_2O were added in 1.5 hrs. with stirring to 137 g. powd. KOH in 250 ml. dry Et_2O with ice cooling; after 7 hrs. at 0° and 2 hrs. at 10°, the washed and Et_2O-extd. product gave 70% *methyl-tert-butyl(vinylethynyl)carbinol*, b_{15} 78-8.5°. This (100 g.) and 100 ml. 62% H_2SO_4 stirred 1 hr. at 45° and 3 hrs. at 63-4°, then extd. with Et_2O and washed with 1% soda soln., gave 66.2% *2-tert-butyl-1,5-hexadien-3-yne* (I), b_{15} 44-5°, n_D^{20} 1.4858. I (31 g.), 75 ml. 90% MeOH, 2 ml. concd. H_2SO_4, and 4 g. Hg sulfate, stirred 10 hrs. at 65° with addn. of 4 g. Hg sulfate in portions every 3 hrs., gave 17.3 g. *1-tert-butyl-3-methyl-1-cyclopenten-5-one* (II), b_{15} 80-8°, b_{10} 71-3°, n_D^{20} 1.4657, d_4^{20} 0.9011, and 5 g. *2-tert-butyl-5-methoxy-1-hexen-3-one* (III), yellow, b_1 82-4°, n_D^{20} 1.4503, d_4^{20} 0.9085; if the starting material is heated 3 hrs. at 60-70° with H_3PO_4 (d. 1.75), complete decompn. to tar takes place. Hydrogenation of II in MeOH over Pt oxide gave *1-tert-butyl-3-methylcyclopentan-5-one*, b_5 51-3°, n_D^{20} 1.4524, d_4^{20} 0.8865; ozonization of II gave HCO_2H, Me_3CCO_2H (b_6 53-5°), and methylsuccinic acid, m. 112°. III (5 g.) and 0.02 g. *p*-$MeC_6H_4SO_3H$ after 3 hrs. at 150° at 200 mm. gave 4 g. *2-tert-butyl-1,5-hexadien-3-one*, green-yellow, b_9 59°, n_D^{20} 1.4630, d_4^{20} 0.8832, which on hydrogenation in MeOH over Adams Pt catalyst gave *2-tert-butylhexanone*, b_9 51-2°, n_D^{20} 1.4317, d_4^{20} 0.8501, while ozonization gave HCO_2H and Me_3CCO_2H. II (2 g.) in 20 ml. 96% EtOH treated in 2 hrs. with 3.6 g. Na gave 1.7 g. *1-tert-butyl-3-methyl-5-cyclopentanol*, colorless, b_6 71°, n_D^{20} 1.4525, d_4^{20} 0.882; 2 g. II refluxed 6 hrs. with MeMgI (from 7.8 g. MeI) in Et_2O gave, after decompn. with dil. HCl and washing with 1% hyposulfite soln., 1 g. *1-tert-butyl-3,5-dimethyl-5-cyclopentanol*, b_7 63-5°, n_D^{20} 1.4518. None of the above ketones contg. a carbonyl adjacent to a *tert*-Bu group gives semicarbazones. LXIX. Transformations of methylphenyl(vinylethynyl)carbinol. *Ibid.* 903-10.—To $CH_2:CHC:CMgBr$ (from 36 g. Mg, 165 g. EtBr, and 80 g. $CH_2:CHC:CH$) in 400 ml. Et_2O was added in 1 hr. with stirring and ice-cooling 120 g. AcPh in 100 ml. Et_2O; after standing overnight, decompn. by 5% HCl gave, on distn. in a N atm. and in small portions, 87% *methylphenyl(vinylethynyl)carbinol* (III), $b_{1.5}$ 102°, m. 37°, n_D^{20} 1.5625; the molten carbinol readily polymerizes to a glassy polymer; hydrogenation in MeOH over a Pt catalyst gave methylphenylbutylcarbinol, b_{15} 119.5-20°, n_D^{20} 1.5112. The carbinol is very sensitive to acids, readily losing water on heating with 50% H_2SO_4, H_3PO_4, or vacuum distn. with small amts. of HCl, AcOH, $KHSO_4$, Ac_2O, or *p*-$MeC_6H_4SO_3H$; because of extremely rapid polymerization it was impossible to isolate the resulting *diene* in pure state: the crude product, after very rapid distn., b_6 98-100°, n_D^{20} 1.6027. The carbinol (12 g.), 100 ml. 90% MeOH, and 1 g. H_2SO_4 after 2 hrs. at 65° gave 8 g. *MeO deriv.* (I), $b_{1.5}$ 77°, n_D^{20} 1.5355, d_4^{20} 0.997, which gradually darkens in the air but can be stored in ampul, although it undergoes slow polymerization; ozonization of the Me ether gave HCO_2H, AcPh, and $(CO_2H)_2$, while hydrogenation in MeOH over Raney Ni gave *methylphenylbutylcarbinol Me ether*, $b_{1.5}$ 70°, n_D^{20} 1.4938, d_4^{20} 0.928. I (20 g.), 300 ml. MeOH, and 10 g. Hg sulfate stirred 2 hrs. at 65° gave 7 g. *1-methoxy-5-phenyl-4-hexen-3-one* (II), b_1 118-20°, n_D^{20} 1.5552. Distn. of 10 g. I and 50 mg. *p*-$MeC_6H_4SO_3H$ at 12 mm. gave 5 g. I mixed with the *dienyne*. To the Grignard reagent (from 23 g. EtI) in 100 ml. Et_2O was added 8 g. $MeBuC(OMe)Ph$ and the mixt. kept 4 hrs. at 60°, then treated with 5% HCl and distd. *in vacuo*, yielding 4 g. *2-phenyl-3-hexene*, b_1 66-8°, b_{750} 224-7°, n_D^{20} 1.5200, d_4^{20} 0.910: the

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same product results when the above ether is distd. at 28 mm. In the presence of p-$MeC_6H_4SO_3H$. III (41 g.), 250 ml. dry MeOH, and 6 g. Hg sulfate, stirred 30 min. at 45°, treated with 6 g. Hg sulfate, and stirred 1 hr. at 65°, gave 8 g. I and 24 g. II, b_2 118-20°, n_D^{20} 1.5553. Stirring 200 ml. MeOH, 80 g. III, and 10 g. Hg sulfate 45 min. at 65° gave 23 g. I and 20 g. II. The latter, a yellowish oil, polymerizes very slowly on standing, and, in pure state, $b_{1.5}$ 117°, n_D^{20} 1.5558, d_4^{20} 1.043; its ozonization gave AcPh, BzOH, HCO_2H, and β-methoxypropionic acid, $b_{1.5}$ 67°, while hydrogenation in MeOH over Pt gave *1-methoxy-3-phenyl-3-hexanone*, b_2 100-7°, n_D^{20} 1.5014, d_4^{20} 0.984. II (26 g.) distd. with 0.02 g. p-$MeC_6H_4SO_3H$ at 2 mm. gave 10 g. green *3-phenyl-1,4-hexadien-3-one*, b_2 107-8°, n_D^{20} 1.5802, d_4^{20} 1.032, which turns red and polymerizes on standing in air; its hydrogenation in MeOH over Raney Ni gave *3-phenyl-3-hexanone*, b_2 66-7°, n_D^{20} 1.5056, d_4^{20} 0.962, while ozonization gave AcPh, HCO_2H, and BzOH. **LXX. Mechanism of hydration and cyclization of dienynes. 14. Hydration and cyclization of 3-phenyl-1,5-heptadien-3-yne.** *Ibid.* 911-16.—To CH_2:CHC:CMgBr (from 30 g. Mg, 165 g. EtBr, and 100 g. CH_2:CHC:CH in 300 ml. Et_2O) was added with cooling and stirring 134 g. PhCOEt in 15 min.; after standing 36 hrs., hydrolysis by 10% HCl with cooling to −15° gave 177 g. *EtPh(HO)CC:CCH:CH₂* (I), b_2 107°, n_D^{20} 1.5500, d_4^{20} 1.007, slowly loses water on standing and in 1 month gives 3-phenyl-3,6-heptadien-4-yne. I (3.28 g.) hydrogenated in MeOH over Pt gave 3.12 g. ethylphenylbutylcarbinol, $b_{1.5}$ 80-90°, n_D^{20} 1.5057, d_4^{20} 0.9465.

I (20 g.) distd. at 10 mm. with 5 g. powd. $KHSO_4$ gave 13.4 g. yellowish *3-phenyl-1,5-heptadien-3-yne* (II), b_{10} 124-5°, $b_{1.5}$ 94°, n_D^{20} 1.5042, d_4^{20} 0.9375, which polymerizes in the presence of air, yields 3-phenylheptane, $b_{1.5}$ 65°, n_D^{20} 1.4870, d_4^{20} 0.859, on hydrogenation in MeOH over Pt, and on ozonization gives HCO_2H, AcOH, and BzOH. II (70 g.) was added to 240 ml. 90% MeOH, 6 ml. concd. H_2SO_4, and 10 g. Hg sulfate, stirred 2 hrs. at 60-5°, then treated with 10 g. Hg sulfate and stirred 2 hrs. longer, yielding 57 g. *3-phenyl-1,5-heptadien-4-one* (III), yellow, $b_{1.5}$ 111-13°, n_D^{20} 1.5543, d_4^{20} 1.013; higher-boiling fractions, $b_{1.5}$ 113-32°, contain some III, 2-methoxy-5-phenyl-5-hepten-4-one, and *1-phenyl-2,3-dimethyl-1-cyclopenten-5-one* (IV), isolated as the *semicarbazone*, m. 204°. III (5 g.) hydrogenated in MeOH over Pt gave 2.4 g. *5-phenyl-4-heptanone*, $b_{1.5}$ 85-8°, n_D^{20} 1.4950, d_4^{20} 0.943; *semicarbazone*, m. 113° (from MeOH). Ozonization of III gave HCO_2H, AcOH, and BzOH. III (10 g.) and 15 ml. H_3PO_4 (d. 1.82) stirred at 60-5° 1.5 hrs. gave 15 g. IV, $b_{1.5}$ 130°, n_D^{20} 1.5725, d_4^{20} 1.0501; *semicarbazone*, m. 204-5° (from EtOH); this on hydrogenation in MeOH over Pt gave *1-phenyl-2,3-dimethylcyclopentanone*, $b_{1.5}$ 110-12°, n_D^{20} 1.5235, d_4^{20} 1.013; *semicarbazone*, m. 173° (from MeOH). IV on ozonization gave AcOH, BzOH, and β-methyllevulinic acid, $b_{1.5}$ 100°, n_D^{20} 1.4501; semicarbazone, m. 176°.

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

FISHER, L. B.

USSR/Chemistry - Acetylene, Derivatives
Chemistry - Isomerization

Jul-Aug 48

"Acetylene Derivatives, No 61," I. N. Nazarov, L. B. Fisher, Inst Org Chem, Acad Sci USSR, 8½ pp

"Iz Ak Nauk, SSSR Otdel Khim Nauk" No 4

Investigates reversible isomerization of 1, 3-hexadiene-5-ol into 2,4-hexadiene-1-ol (sorbic Alcohol) under the influence of dilute sulfuric acid. Investigates reaction of hydrogen chloride with these two diene alcohols and also hydrolysis and acetylization of the chlorides thus obtained. Describes reversible regrouping of 1,3-diene system observed in the exchang reactions mentioned. Submitted 7 Jun 1947

PA 8/49T17

FISHER, L. B.

USSR/Chemistry - Acetylebe, Derivitives
Chemistry - Hydrogenation

Jul/Aug 48

"Acetylene Derivatives, No 81," I. N. Nazarov, L.B. Fisher, Inst Org Chem, Acad Sci, USSR, 8¼ pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4.

Describes hydrogenation of phenyl-vinylethylene-carbinol (I) into 5-phenyl, 3-pentadiene-5-ol (II) by means of copperized zinc dust and water. Achieved irreversible isomerisation of 5-phenyll-1, 3-pentadiene-5-ol into 5-phenyl-2, 4 pentadiene-1-ol (III) by the action of diluted sulfuric acid. Investigated action of hydrogen chloride on diene alcohols II and III, and also the hydrolysis and esterification of the primary chloride thus obtained. Submitted 6 Jun 1947.

PA 8/49T18

B.A.

A II -1

Derivatives of acetylene. CXI. Rearrangements of polyene systems. VI. Allyl and triene isomerisations of hepta-1 : 6-dien-3-yn-5-ol, hepta-1 : 3 : 6-trien-5-ol, and octa-1 : 3 : 6-trien-5-ol. I. N. Nazarov and L. B. Fisher (*J. gen. Chem. USSR*, 1950, 20, 1107—1113 (U.S. transl., 1149—1155); cf. Heilbron, Jones, and McCombie, A., 1944, II, 177).—The action of $CH_2{:}CH{\cdot}C{:}C{\cdot}MgBr$ on acrolein gives a 55% yield of $CH_2{:}CH{\cdot}C{:}C{\cdot}CH(OH){\cdot}CH{:}CH_2$, which, upon shaking with 3% H_2SO_4 at 70° is completely isomerised to $CH_2{:}CH{\cdot}C{:}C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH$. The former alcohol is smoothly hydrogenated by means of Cu-treated Zn dust and H_2O to give the triene alcohol $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH{:}CH_2$, which is easily isomerised with 1% H_2SO_4 at room temp. to $CH_2{:}CH{\cdot}[CH{:}CH]_2{\cdot}CH_2{\cdot}OH$. Similarly, the dienyne alcohol, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C{:}CMe$, formed in 75% yield by the action of $CH_2{:}CH{\cdot}C{:}C{\cdot}MgBr$ on crotonaldehyde, is smoothly hydrogenated to the triene alcohol $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH{:}CHMe$, which is isomerised with 1% H_2SO_4 at room temp. to $CH_2{:}CH{\cdot}[CH{:}CH]_2{\cdot}CHMe{\cdot}OH$. Upon shaking this with 1% H_2SO_4 at room temp., it undergoes a slow reversible isomerisation to the primary triene alcohol $OH{\cdot}CH_2{\cdot}[CH{:}CH]_3{\cdot}Me$. Upon reduction of $CH_2{:}CH{\cdot}C{:}C{\cdot}CH(OH){\cdot}CH{:}CHMe$ with Zn dust and water, there is obtained, in addition to $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}CH{:}CHMe$, a small yield (about 3%) of $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CHMe$ or $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CHEt$, formed by reduction of the hydroxyl group.

Vinylacetylene (60), EtBr (130), and Mg (22 g.), are mixed in Et_2O to give $CH_2{:}CH{\cdot}C{:}C{\cdot}MgBr$ (I), which is stirred continuously in a current of N_2 at −16°, whilst acrolein (50 g.) in Et_2O (50 ml.) is added over 30 min. After standing overnight, the Grignard complex is decomposed with ice and saturated aq. NH_4Cl under N_2, giving *hepta*-1 : *6-dien-3-yn-5-ol*, C_7H_8O (II) (52 g.), b.p. 77—78°/16 mm., d_4^{20} 0·9354, n_D^{20} 1·5040. Hydrogenation of II in EtOH, in the presence of Pt gives CHEtBu·OH, b.p. 152—154°, which is oxidised by CrO_3 in AcOH to COEtBu, b.p. 145—146° (semicarbazone, m.p. 106—107°). II (6 g.) and 3% H_2SO_4 (60 ml.) are stirred together under N_2 at 65—70° for 6 hr. to give *hepta*-1 : 5-*dien-3-yn-7-ol*, C_7H_8O (III) (3·3 g.), b.p. 75—76°/3 mm., d_4^{20} 0·9515, n_D^{20} 1·5520, which forms a gelatinous polymer on keeping for 7 days. Upon hydrogenation, III gives n-$C_7H_{15}{\cdot}OH$, b.p. 78—79°/15 mm. (phenylurethane, m.p. 59—60°). II (43 g.), Cu-treated Zn dust (21 g.), Et_2O (75 ml.), and H_2O (10 ml.) are stirred for 12 hr. at 30—32°; then 4 more lots of 21 g. of Cu-treated Zn dust and 10 ml. of H_2O are added. The experiment takes 11 days and stirring is continued for 123 hr. The product is *hepta*-1 : 3 : 6-*trien-5-ol*, $C_7H_{10}O$ (IV) (30 g.), b.p. 68—70°/16 mm., d_4^{20} 0·8959, n_D^{20} 1·4995. Hydrogenation of IV gives CHEtBu·OH, b.p. 150—152°. IV (9 g.) in 60% aq. dioxan (75 ml.), containing 1% H_2SO_4, is shaken for 3 hr. under N_2 at room temp., then Et_2O is added, and the product salted out with KOH, giving *hepta*-1 : 3 : 5-*trien-7-ol*, $C_7H_{10}O$ (V) (3·6 g.), m.p. 79—80°, b.p. 65—68°/3 mm. Upon hydrogenation, V gives n-$C_7H_{15}{\cdot}OH$, b.p. 78°/15 mm. (phenylurethane, m.p. 58—60°). I in Et_2O is treated with crotonaldehyde at −15° to give octa-1 : 6-dien-3-yn-5-ol (VI), b.p. 67—68°/3 mm., n_D^{20} 1·5070 (cf. Heilbron, *et al.*, *loc. cit.*). VI (184 g.), Cu-treated Zn dust (52 g.), Et_2O (400 ml.), and H_2O (30 ml.) are stirred for

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BA

Derivatives of acetylene. CXII. Rearrangements of polyene systems. VII. Synthesis and isomerisation of styrylvinylethynylcarbinol, styrylbutadienylcarbinol, furylvinylethynylcarbinol, and furylbutadienylcarbinol. I. N. Nazarov and L. B. Fisher (J. gen. Chem. USSR, 1950, 20, 1114 et seq. [U.S. transl., 1157—1167]; cf. A., 1946, II, 632, and preceding abstract).—The action of $CH_2:CH\cdot C:C\cdot MgBr$ on cinnamaldehyde gives styryl(vinylethynyl)-carbinol [3-hydroxy-1-phenylhepta-1 : 6-dien-4-yne] in 84% yield. Under the action of 3% H_2SO_4 in aq. dioxan, this isomerises to $CH_2:CH\cdot C:C\cdot CH:CH\cdot CHPh\cdot OH$. Upon hydrogenation with Cu-treated Zn dust and H_2O, $CH_2:CH\cdot C:C\cdot CH(OH)\cdot CH:CHPh$ is transformed fairly smoothly into $CH_2:CH\cdot CH:CH\cdot CH(OH)\cdot CH:CHPh$, which, under the influence of 1% H_2SO_4 in aq. dioxan solution, is also isomerised irreversibly into $CH_2:CH\cdot CH:CH\cdot CH:CH\cdot CHPh\cdot OH$. Under the action of dil. H_2SO_4, this last undergoes further triene isomerisation, the OH shifting from $C_{(7)}$ to form a primary triene alcohol, $OH\cdot CH_2\cdot[CH:CH]_3\cdot Ph$. This isomerisation takes place less readily than in the case of the analogous alcohols with Me groups. The action of $CH_2:CH\cdot C:C\cdot MgBr$ on furfural gives α-furyl(vinylethynyl)-carbinol in 66% yield. By means of Cu-treated Zn dust, this is hydrogenated to give α-furylbutadienylcarbinol. All attempts to carry out isomerisations on these compounds have been unsuccessful, as a result of their extreme instability, and their tendency to form tar. Hydrogenation of $CH_2:CH\cdot C:C\cdot CH(OH)\cdot CH:CHPh$ with Cu-treated Zn dust and H_2O also gives phenylheptatriene $(CH_2:CH\cdot CH:CH\cdot CH_2\cdot CH:CHPh$ or $CH_2:CH\cdot[CH:CH]_2\cdot CH_2Ph)$, formed as a result of the reduction of the OH in $CH_2:CH\cdot CH:CH\cdot CH(OH)\cdot CH:CHPh$.

$CH_2:CH\cdot C:C\cdot MgBr$ (I) in Et_2O is treated with cinnamaldehyde in the usual manner (cf. preceding abstract) to give *styryl(vinylethynyl)carbinol* [*3-hydroxy-1-phenylhepta-1 : 6-dien-4-yne*], $C_{13}H_{12}O$ (II), b.p. 140—141°/2 mm., d_4^{20} 1·0394, n_D^{20} 1·6005. It is necessary to distil the product in small batches of 10 g. at a time, at low pressure, under N_2, to avoid decomposition. II is hydrogenated in EtOH in the presence of Pt to give *1-phenylheptan-3-ol*, $C_{13}H_{20}O$ (III), b.p. 136—138°/7 mm., d_4^{20} 0·9446, n_D^{20} 1·5040, which is oxidised with CrO_3 in AcOH to $COBu^n\cdot[CH_2]_2\cdot Ph$, b.p. 125—128°/7 mm., d_4^{20} 0·9391, n_D^{20} 1·4980 (*2 : 4-dinitrophenylhydrazone*, $C_{19}H_{22}O_4N_4$, m.p. 130—132°). II is shaken with 70% aq. dioxan containing 3% of H_2SO_4, and heated for 12 hr. at 45° in a current of N_2 in the presence of pyrogallol. Distillation of the product yields *1-phenylhepta-2 : 6-dien-4-yn-1-ol*, $C_{13}H_{12}O$ (IV), b.p. 139—141°/2 mm., d_4^{20} 1·0386, n_D^{20} 1·6002. IV is hydrogenated in the presence of Pt to 1-phenylheptan-1-ol, b.p. 135—138°/7 mm., which is oxidised to 1-phenylheptan-1-one, b.p. 129—131°/7 mm. (semicarbazone, $C_{14}H_{21}ON_3$, m.p. 118—119°; 2 : 4-dinitrophenylhydrazone, m.p. 137—139°), also obtained by the Grignard reaction of PhCHO with $C_6H_{13}Br$. II is reduced with Cu-treated Zn dust in the same manner as before to give, after 3 distillations, fractions of b.p. 120—130°/2 mm., n_D^{20} 1·6160, and b.p. 130—131°/2 mm., n_D^{20} 1·5970, both predominantly *1-phenylhepta-1 : 4 : 6-trien-3-ol*, $C_{13}H_{14}O$ (V), b.p. 130—131°/2 mm., d_4^{20} 1·0210, n_D^{20} 1·5970: the former contains some phenylheptatriene as impurity. If the reaction is conducted at 35—40°, the main product is *1-phenylhepta-2 : 4 : 6 (or 1 : 4 : 6)-triene*, $C_{13}H_{14}$ (VI), b.p. 108—110°/2 mm., n_D^{20} 1·6330. V is hydrogenated in EtOH in the presence of Pt, to give 1-phenylheptan-3-ol (VII), b.p. 135—137°/7 mm., which is oxidised with CrO_3 in AcOH to $COBu^n\cdot[CH_2]_2\cdot Ph$. VI is similarly reduced to 1-phenylheptane, b.p. 89—100°/8 mm. d_4^{20} 0·2565, n_D^{20} 1·4870. V is shaken in N_2 with 70% aq. dioxan containing 1% H_2SO_4 for 1 hr. at 45° in the presence of pyrogallol. The product obtained is a mixture, b.p. 130—142°/2 mm., n_D^{20} 1·6062 of V and pure *1-phenylhepta-2 : 4 : 6-*

(over)

FISHER L.B.

27

4

Preparation of activated alumina from the Tr[illegible] [illegible]

FISHER, L. B.

KOTLYAREVSKIY, I.L.; FISHER, L.B.

Hydrogenation of gaseous olefins under pressure. Zhur. prikl. khim. 29 no.11:1756-1757 N '56. (MIRA 10:6)

1. Laboratoriya organicheskogo sinteza Vostochno-Sibirskogo filiala Akademii nauk SSSR.
(Hydrogenation) (Olefins)

FISHER, L.B.; BELEN'KAYA, A.P.; MARUSHKIN, M.N. [deceased].

Catalytic dehydrogenation of butane to butene over catalysts obtained from local raw materials. Izv. vost. fil. AN SSSR no.1:53-59 '57.
(MIRA 11:4)

1. Vostochno-Sibirskiy filial AN SSSR.
(Butane) (Dehydrogenation) (Kaolin)

FISHER, L.B.; TERPUGOVA, M.P.; KOTLYAREVSKIY, I.L.

Catalytic dehydrogenation of 2,3-dimethylbutane. Izv. vost. fil. AN SSSR no.9:53-56 '57. (MIRA 11:1)

1. Vostochno-Sibirskiy filial AN SSSR.

(Butane) (Dehydrogenation)

AUTHOR: Fisher, L. B. (Irkutsk) 74-27-5-3/6

TITLE: Amines of the Acetylene Series (Aminy atsetilenovogo ryada)

PERIODICAL: Uspekhi Khimii, 1958, Vol. 27, Nr 5, pp. 589-621 (USSR)

ABSTRACT: In the introduction the author points out that beside the classic methods of synthesis of acetylene-amines methods based upon Mannich's reaction (reaktsiya Mannikha) recently gained importance. In the years before World War Two a great number of processes was worked out which are based upon the reaction of acetylene with ammonia and with amines. Later the works in this field were intensively continued. Then in the present paper the methods are discussed in individual sections: the catalytic methods, the method of the synthesis of acetylene-amines (according to Repps, references 12 - 15), further the synthesis of aminobutynes published in 1949. A special section is devoted to Mannich's reaction. Among others it is pointed out that Marshak and his collaborators in the investigation of the conditions of the synthesis of tertiary acetylene-amines by means of Mannich's reaction found that an excess of formaldehyde must be obtained at the end of the

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reaction. Further data on the mechanism of the reaction of acetylene compounds with amines and formaldehydes follow. The works by Dornow and Ishe (reference 43), Marszak (references 44, 19, 41, 45, 46), Nazarov, and Shvekhgeymer (reference 54) are discussed. A special section deals with the problem of the production of acetylene-amines by means of substitution reactions and so-called mixed methods. The works by Hennion and Teach (reference 66), Marszak and Kulkes (reference 69), as well as Petrayev (reference 78, 79) are referred to. The next section deals with the properties and the use of acetylene-amines. The author discusses the production of a number of disubstituted tertiary acetylene-amines by the condensation of sodium-substituted diethyl-aminopropyne with different haloid alkyls, whereby a number of dimethylaminoalkanes could be synthesized (Parsell and Pollard, reference 84). The author also describes the synthesis of primary, secondary, and tertiary amino-alcohols by means of the interaction of monosubstituted aminoacetylene compounds with organic oxides, aldehydes and ketones in the presence of sodium amide in liquid ammonia. Then follows an

enumeration of further syntheses: The production of new acetylene-1,4-aminoalcohols, of acetylene-aminoesters and other compounds. The isomerization of N-substituted compounds of 2-aminobutyne-3 to N-substituted 2-aminobutadiene-1,3 derivatives; the hydrogenation of acetylene and its derivatives is described in detail. The 24 tables added to the paper offer a good survey. There are 24 tables, 108 references, 25 of which are Soviet.

1. Acetylene derivatives--Synthesis

FISHER, L.B.; TERPUGOVA, M.P.; KOTLYAREVSKIY, I.L.

Dehydrogenation of butane di-derivatives; studying the first stage of 2,3-dimethylbutane dehydrogenation. Izv.Sib.otd. AN SSSR no.9:32-38 '58. (MIRA 11:11)

1. Vostochno-Sibirskiy filial Akademii nauk SSSR.
(Butane) (Dehydrogenation)

5(1,3) SOV/153-2-4-26/32

AUTHORS: Kotlyarevskiy, I. L., Fisher, L. B., Zanina, A. S., Terpugova, M. P., Volkov, A. N., Shvartsberg, M. S.

TITLE: Synthesis of Several Monomers on Alumochromium Catalysts

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 4, pp 608 - 613 (USSR)

ABSTRACT: A report on this paper was given at the All-Union Conference on "Ways of Synthesis of Initial Products for the Production of High Polymers" which took place in Yaroslavl' from September 29 to October 2, 1958. The results of the catalytic synthesis of 2,3-dimethyl-butadiene-1,3 as well as of monomers of the type of p-xylene from acetylene derivatives are given. The substance mentioned at first can be used in the production of special rubber types (Ref 1). It could not be obtained by the production methods so far used. The diagram (see Diagram) being worked at by the authors consists of two stages. The first one (Ref 2) yielded not more than 15% of the end product. In spite of numerous patents (Ref 3), a thorough description of reaction conditions is still missing. Therefore, the authors determined the optimum conditions of isobutane alkylation with ethylene

in the presence of aluminum chloride. Under these conditions (48 - 51°, 7 - 9 atm, 1.5 kg isobutane, 145 g ethylene, 40 g C_2H_5Cl, 5 g $AlCl_3$, 2 hours) the yield of 2,3-dimethyl-butane rises to 47%. The reaction is very sensitive to temperature (only 1/3 of the alkylate yield at 35°). The catalyst can be used 5 to 6 times without reducing the quantity of alkylate or of 2,3-dimethyl-butane. Ethylene has to be added during the whole process: its partial pressure must not exceed 0.5 - 0.7 atm, or otherwise the 2,3-dimethyl-butane content in the alkylate decreases rapidly. The addition of 1-3% C_2H_5Cl accelerates the process. Isobutane alkylation with ethylene at a high temperature proceeds at a pressure of 100 - 200 atm according to a radical mechanism, and is accelerated by radical donors. It was carried out by the authors in the presence of C_2H_5Cl (for the first time) in a special, continuously working plant. The alkylate yield (computed for ethylene) reached 170-180% under optimum conditions (450°, 200 atm, reaction time 25 minutes, weight ratio isobutane : ethylene = 10 : 1, initiator quantity 2.5%). 2,2-Dimethyl-butane (32-35% of the alkylate) was the

main product; 2,3-dimethyl-butane amounted to 8-10% of the alkylate. The preparation of 2,3-dimethyl-butadiene-1,3 from 2,3-dimethyl-butane proceeds in two stages: a) Dehydration with the formation of two olefines: 1) tetramethyl-ethylene, and 2) 2,3-dimethyl-butene-1. b) Dehydration of the olefines to the end product. This reaction has not been considered in publications (except for the reference in the patent (Ref 5)). The authors investigated the first stage thoroughly on an alumochromium-potassium catalyst. The specifications for its production were provided by M. N. Marushkin (deceased) (IOKh AN SSSR = Institute of Organic Chemistry AS USSR). This catalyst showed the highest activity at 550°. The catalyzate reached a 87% yield with a content of unsaturated hydrocarbons of 60-67%. The investigation of the second stage has not yet been completed. An aromatization diagram of divinyl-acetylene-hydrocarbons is given. Several mono-, bi-, and tricyclic hydrocarbons with a prescribed structure were produced on the basis of the diagram. A diagram of the reactions of the synthesis of p-xylene from acetylene and acetone is suggested. Since there is no demand for acetone in the USA because of increasing phenol production,

and its price according to the Sergeyev method is already 1/3 - 1/4 of the present one, the synthesis method mentioned above might become useful for industry. In conclusion, a simple way of synthesis for polyphenyl systems is suggested. Moreover, the Favorskiy reaction is mentioned in the paper. There are 11 references, 5 of which are Soviet.

ASSOCIATION: Vostochno-Sibirskiy filial SO AN SSSR (East Siberian Branch of the Siberian Department of the Academy of Sciences, USSR)

KOTLYAREVSKIY, I.L.; VOLKOV, A.N.; FISHER, L.B.

Laboratory method for producing 2,3-dimethylbutane by the alkylation of isobutane by ethylene. Izv. Sib. otd. AN SSSR no.3:62-66 '59. (MIRA 12:8)

1. Vostochno-Sibirskiy filial Sibirskogo otdeleniya Akademii nauk SSSR.
(Butane) (Ethylene) (Alkylation)

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000413310008-1"

KOTLYAREVSKIY, I.L.; VOLKOV, A.N.; FISHER, L.B.

Alkylation of butane and isobutane by ethylene. Izv.Sib.otd. AN SSSR no.4:64-70 '59. (MIRA 12:10)

1. Vostochno-Sibirskiy filial Sibirskogo otdeleniya Akademii nauk SSSR.
(Butane) (Ethylene) (Alkylation)

KOTLYAREVSKIY, I.L.; FISHER, L.B.; ZANINA, A.S.; TERPUGOVA, M.P.;
VOLKOV, A.N.; SHVARTSBERG, M.S.

Synthesis of some monomers over aluminochromium catalysts.
Izv.vys.ucheb.zav.; khim.i khim.tekh 2 no.4:608-613
'59. (MIRA 13:2)

1. Vostochno-Sibirskiy filial Sredneaziatskogo otdeleniya
AN SSSR.
(Butadiene) (Catalysis)

FISHER, L.B. ; TERPUGOVA, M.P.; KOTLYAREVSKIY, I.L.

Dehydrogenation of disubstituted butanes. Dehydrogenation of 2,3-dimethylbutane and 2,3-dimethylbutenes in the presence of diluents. Izv.Sib.otd.AN SSSR no.2:57-60 '61. (MIRA 14:3)

1. Vostochno-Sibirskiy filial Sibirskogo otdeleniya AN SSSR, Irkutsk.

(Butane) (Butene) (Dehydrogenation)

25278
S/062/61/000/010/015/018
B106/B101

15.8063

AUTHORS: Kotlyarevskiy, I. L., Fisher, L. B., and Domnina, Ye. S.

TITLE: Oxidative polycondensation of diacetylene compounds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1961, 1905 - 1907

TEXT: In a previous paper (Ref. 1: I. L. Kotlyarevskiy, L. B. Fisher, A. A. Dulov, A. A. Slinki, Izv. AN SSSR. Otd. khim. n. 1960, 950) the example of p-diethynvl benzene (I) showed that oligomers with conjugate aromatic and acetylene bonds can be obtained by oxidative condensation to linear diacetylene compounds. After this paper, another one describing a similar synthesis was published (Ref. 2: see below). The physical properties of the poly-p-diethynyl benzene thus synthesized are similar to those of semiconductors and ferromagnetics. In the present paper, the examination of this reaction is continued. The corresponding polymers for which, in analogy to II, the structures VII, VIII, IX, and X are suggested, were obtained by oxidative polycondensation of 1,4-diethynyl-1,4-dihydroxy-cyclohexane (III), 9,10-diethynyl-9,10-dihydroxy-9,10-dihydro
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B106/B101

Oxidative polycondensation of...

anthracene (IV), 9,10-diethynyl-9,10-dihydroxy-9,10-dihydro phenanthrene (V), and 9,10-diethynyl anthracene (VI).

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25276
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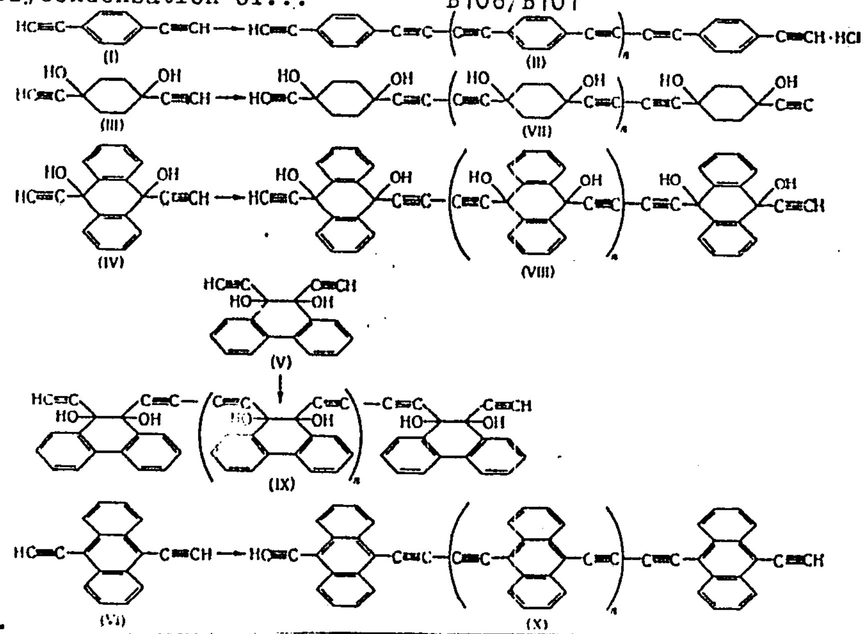
B106/B101

Oxidative polycondensation of...



Card 3/6

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Oxidative polycondensation of... S/062/61/000/010/015/018
B106/B101

The initial p-diethynyl benzene (I) was obtained by two methods: (1) from the dehydrogenation products of p-diethyl benzene (Ref. 4: A. A. Balandin, N. I. Shuykin, G. M. Marukyan, I. I. Brusov, R. G. Seymovich, G. K. Lavrovskaya, V. K. Mikhaylovskiy, Zh. prikl. khimii, 32, No. 11, 2566, 1959), which were brominated in carbon tetrachloride at -12 - -15°C. The resulting tetrabromide was filtered off, washed with carbon tetrachloride, and recrystallized from chloroform (melting point: 156 - 157°C). Hydrogen bromide was then split off from the above tetrabromide by a method of R. Deluchat (Ref. 7: Ann. chimie 11, 1, 181 (1934)), and p-diethynyl benzene (melting point: 95°C) was thus obtained. 2) From p-diacetyl benzene by catalytic hydrogenation to 1,4-di(-1-hydroxy-ethyl)-benzene, by dehydration to p-divinyl benzene, and by bromination and further treatment of the latter as described under 1). The monomers III - V were obtained by condensation of acetylene and diketones in liquid ammonia (Ref. 5: W. Ried, H. J. Schmidt, Chem. Ber. 90, 2499 (1957)). Compound VI was obtained by aromatization of IV (Ref. 6: W. Ried, H. J. Schmidt, A. Urschel, Chem. Ber. 91, 2472 (1958)). Cuprous chloride was used as a catalyst for polycondensation, and aqueous dioxane, aqueous alcohol, and pyridine (Ref. 2: see below) were used as solvents. The

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B106/B101

Oxidative polycondensation of...

solution of the catalyst and of the corresponding monomer in the solvent used was shaken together with oxygen at room temperature until gas absorption came to an end. The reaction mixture was decomposed with water, and the deposited product was washed with water until the chloride was removed. Oligomer II is orange-red (at n = 6) or bright-yellow (at n = 5), and insoluble in water and conventional organic solvents. Oligomer VII is bright-colored, polymers VIII and IX are darkish brown powders, and polymer X is black. These polymers are all insoluble in conventional organic solvents at room temperature. Compounds VIII and IX contain traces of copper but no chlorine, and polymer X contains chlorine. There are 8 references: 3 Soviet and 5 non-Soviet. The two references to English-language publications read as follows: Ref. 2: A. S. Hay, J. Organ. Chem. 25, 1275 (1960); C. A. Hochwalt, Pat. USA 2390368 (1954); Chem. Abstrs, 1878 (1946).

ASSOCIATION: Institut khimii Sibirskogo otdeleniya Akademii nauk SSSR (Institute of Chemistry of the Siberian Department of the Academy of Sciences USSR)

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Card 5/6

33374
S/190/62/004/002/002/021
B110/B101

15.8340

AUTHORS: Kotlyarevskiy, I. L., Fisher, L. B., Dulov, A. A., Slinkin, A. A., Rubinshteyn, A. M.

TITLE: Synthesis and some physical properties of poly-p-diethynyl benzene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1962, 174 - 181

TEXT: Poly-p-diethinyl benzene with alternating ternary bonds and phenylene rings was synthesized from p-diethinyl benzene according to Yu. S. Zal'kind (Zh. obshch. khimii, 6, 530, 1936). The diethyl benzene mixture obtained during styrene production was dehydrogenated to divinyl benzene, brominated, dehydrobrominated, and polycondensed in water-alcohol or water-dioxane at 20 - 40°C in the presence of CuCl, NH_4Cl, and O_2 to orange-red, powdery oligomer (I) insoluble in water and organics:

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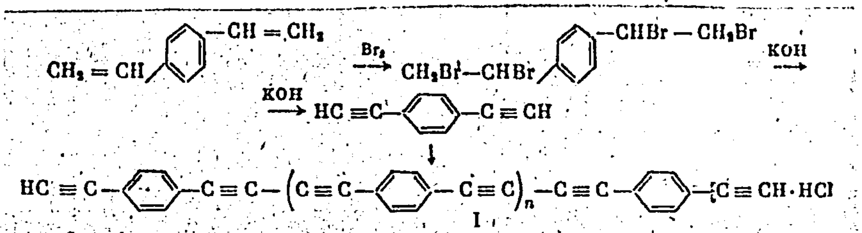
Synthesis and some physical...



$n = 3 - 4$

It explodes under rapid heating to 120 - 130°C in N_2 flow, but is no longer explosive in the form of pressed tablets up to 140°C in N_2 flow. Thermogravimetric and quantitative studies showed that the color change (to black) at 400°C was not due to decomposition but to intramolecular polymerization and structuration processes. The conductivity of tablets pressed at 5000 atm was examined with direct current at $5 \cdot 10^{-3}$ mm Hg. The tablets were heated in N_2 flow for 20 hr. The conductivity is described by: $\sigma = \sigma_0 \exp(-E/kT)$. Resistance and activation energy of conductivity decrease with increasing heating temperature (220 - 600°C) $\sigma \approx 10^{-2}$ $ohm^{-1} \cdot cm^{-1}$; E≈0.1 ev at 600°C). Ultraviolet irradiation of a sample heated at 220°C raises the conductivity

Card 2/5

reversibly by some orders. This effect decreases with increasing heating temperature (400°C) and disappears at 500 and 600°C completely. The sign of the thermo-emf and the reversible resistance decrease during oxygen adsorption confirm the hole character of the conductivity. The specific magnetic susceptibility of the initial oligomer determined between 20 and 160°C at H = 3500 - 4500 oersteds was $\chi = -0.4 \cdot 10^{-6}$, after pressing at 5000atm: $\chi = -0.2 \cdot 10^{-6}$. The maximum number of unpaired electrons exists on heating to 220°C, maximum χ value at 400°C, while ferromagnetic H dependence on χ was observed. The intensities of the epr signal as dependent on heating (2 hrs) in vacuo and N_2 (0.5% O_2) pass through a maximum at ~220°C. X-ray studies with an УРС-55(URS-55) device showed increasing crystal formation (favored by pressing) with increasing heating temperature. The electric and magnetic properties of slightly heated amorphous samples are determined by individual unpaired electrons and energetic barriers between the loosely bound, conjugated sections while ultraviolet irradiation increases the number of current carriers. At higher temperatures, the individual conjugated sections are combined to microcrystalline domains, and the number of electrons which have not yet entered the domain of strong interaction

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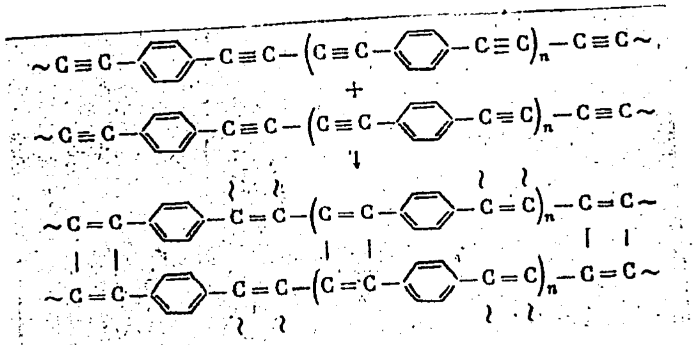
Synthesis and some physical...

decreases. At a certain stage, further crystal growth gives rise to formation of diamagnetic graphite structures. At 400, 500, 600°C, electric resistance and activation energy of conductivity decrease with increasing heating temperature due to the presence of strongly interacting electrons. Two types of structurally different polymers are likely to exist. The conversion of the orange-colored, explosive initial polymer at 200°C is likely to proceed according to:



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Card 4/5

33374

Synthesis and some physical...

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B110/B101

At higher temperatures, domains are formed with ferromagnetic electron interaction due to cross linking which are superposed by diamagnetic interaction on further crystallization. Tal'roze is mentioned. There are 4 figures, 4 tables, and 14 references: 11 Soviet and 3 non-Soviet. The two references to English-language publications read as follows: A. S. Hay, J. Org. Chem., 25, 1275, 1960; D. D. Eley et al., Disc. Faraday Soc., 28, 55, 1959.

X

ASSOCIATION: Institut khimii Vostochno-sibirskogo filiala AN SSSR (Institute of Chemistry of the East Siberian Branch AS USSR). Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: January 30, 1961

Card 5/5

APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000413310008-1"

KHAGANOV, Ye.I., otv. red.; FISHER, L.B., red.; POPOV, K.V., red.; STENNIKOV, M.G., tekhn. red.

[Materials for the conference of young scientists; on the tenth anniversary of the East-Siberian Branch of the Academy of Sciences of the U.S.S.R.] Materialy k konferentsii molodykh nauchnykh sotrudnikov; k 10-letiiu Vostochno-Sibirskogo filiala AN SSSR. Blagoveshchensk. No.3. [Chemistry and metallurgy] Khimiia i metallurgiia. 1960. 93 p. (MIRA 17:2)

1. Akademiya nauk SSSR. Vostochno-Sibirskiy filial, Irkutsk.

EPA(s)-2/EWT(m)/EPF(c)/EPR/EWP(j)/T Pc-4/Pr-4/Ps-4/Pt-10 RPL

ACCESSION NR: AP4041169 S/0062/64/000/006/1090/1095

AUTHOR: Fisher, L. B.; Kotlyarevskiy, I. L.; Domnina, Ye. S.; Trotsenko, Z. P.

TITLE: Highly unsaturated polymers. Communication 9. Synthesis and polycondensation of diacetylenic derivatives of phenanthrene

SOURCE: AN SSSR. Izv. Seriya khimicheskaya, no. 6, 1964, 1090-1095

TOPIC TAGS: diacetylenic polymer, diacetylenic phenanthrene derivative, synthesis, polycondensation, unsaturated polymer, acetylenic oligomer, conjugated acetylenic polymer, conjugated polymer, organic semiconductor, semiconducting polymer

ABSTRACT: As a continuation of research to determine the effects of monomer structure on the physical properties of oligomers, oligomers were synthesized in which conjugation was retained or interrupted, and copolymers were synthesized in ... conjugation alternated with saturated units. ... having interrupted conjugation alternated with saturated units ... was made from ... methoxy-9,10-diethynyl-9,10-dihydrophenanthrene ... 9,10-dihydroxy-9,10-dihydrophenanthrene ... and dimethyl sulfate

Card 1/2

ACCESSION NR: AP4041169

6

and powdered KOH; 9,10-diethynylphenanthrene (II) was made by aromatizing III. [illegible] II were subjected to oxidative polycondensation in pyridine with catalyst [illegible] chloride. Copolymers of I and II, and of I and [illegible] diethynylbenzene (IV), and of III and IV were similarly made. The IR spectra and EPR data for the products are tabulated. "Electron paramagnetic resonance spectra were [illegible] obtained in the laboratory by V. V. Voyevodsko, V. K. Yermolayev, N. M. Gazhin [illegible] Shapovalov, whom the authors thank." Orig. art. has [illegible] tables and 2 sets of equations.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR (Institute of Chemical Kinetics and Combustion Siberian [illegible])

SUBMITTED: 21Nov62 ENCL: 00 SUB CODE: OC

NO REF SOV: 003 OTHER: 001

Card 2/2

FISHER, L.B.; KOTLYAREVSKIY, I.I.; DOMNINA, Ye.S.; TROTSENKO, Z.P.

Highly unsaturated polymers. Report No.9: Synthesis and poly-condensation of diacetylene derivatives of phenanthrene. Izv. AN SSSR. Ser. khim. no.6:1090-1095 Je '64.

(MIRA 17:11)

1. Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.

FISHER, L.B.; KOTLYAREVSKIY, I.L.; ANDRIYEVSKAYA, E.K.

Mannich reaction with p-diethynylbenzene derivatives. Izv. AN SSSR. Ser. khim. no.8:1543-1545 Ag '64. (MIRA 17:9)

1. Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.

L 54448-65 EWT(m)/EPF(c)/EWP(j)/T Pc-4/Pr-4 RM

ACCESSION NR: AP5012453 UR/0062/65/000/004/0692/0697
547.362+541.6

27
26
B

AUTHORS: Fisher, L. B.; Kotlyarevskiy, I. L.

TITLE: Highly unsaturated polymers. Communication 11. Monohydric and dihydric alcohols derived from para-diethynylbenzene

SOURCE: AN SSSR. Izvestiya. Seriya khimicheskaya, no. 4, 1965, 692-697

TOPIC TAGS: unsaturated compound, alcohol, benzol, condensation reaction, organic synthesis, IR spectrum

ABSTRACT: The behavior of paradiethynylbenzene in the Newland reaction was studied. Since acetylene reacts with sodium and sodium amide in liquid ammonia to form a monosodium derivative that will not react further with sodium (or $NaNH_2$) because ... complete saturation, the Newland reaction permits production of ... acetylene alcohols without ... diacetylene ... differently, yielding two series of derivatives: ... and glycols. To investigate the behavior of para-diethynylbenzene in the Newland reaction, the authors undertook condensation of the compound with acetone, cyclohexanone, and benzophenone. In all cases a principal product (70-80%) was glycol (in addition

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ACCESSION NR: AP5012453

to monohydric acetylene alcohol). Under most favorable conditions for glycol ... g-equiv sodium per mole of para-diethynylbenzene and excess of ... the main product was not glycol but carbinol. Apparently an ... is attained between diacetylene and carbinol ... on the one hand ... between these and the dianone on the other, a relation that always leads to ... production of both glycol and alcohol. In order to obtain a reaction ... alcohol formation over glycol, the alcohol obtained by condensation of ... with para-diethynylbenzene was used to obtain ... of the latter. ... resulting product gives a narrow signal on the electron paramagnetic resonance ... The authors attempted to destroy the polyacetylene chain of para-... benzene by the reverse Favor reaction, but results were negative. The ... spectrum of the resulting product shows bands characteristic of both alcohol and glycol. The band of the valence oscillation ... is very weak. The composition and properties of the compounds obtained are tabulated. Orig. art. has: 2 tables and 8 formulas.

ASSOCIATION: Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya, Akademii nauk SSSR (Institute of Chemical Kinetics and Combustion, Siberian Department of the Academy of Sciences, SSSR)

SUBMITTED: 17Apr63 ENCL: 00 SUB CODE: OC, GC

NO REF SOV: 005 OTHER: 003

Card 2/2

L 2352-66 EWT(1)/EWT(m)/EPA(w)-2/T/EWP(t)/EWP(b)/EWA(m)-2/EWA(c) IJP(c) JD/AT

ACCESSION NR: AP5016286 UR/0386/65/001/005/0054/0057

56

AUTHOR: Sharvin, Yu. V.; Fisher, L. M. 44,55

50

B

TITLE: Observation of focused electron beams in a metal

SOURCE: Zhurnal eksperimental'noy i tekhnicheskoy fiziki. Pis'ma v redaktsiyu. Prilozheniye, v. 1, no. 5, 1965, 54-57

TOPIC TAGS: electron beam, electron motion, electron spectrum

ABSTRACT: The authors have performed the experiment proposed by one of them earlier (Sharvin, ZhETF v. 48, 984, 1965), aimed at producing and observing in a metal with large mean free path electron beams starting from a definite point of the sample and focused by longitudinal magnetic field in another point of the sample. A diagram of the experiment is shown in Fig. 1 of the Enclosure. The experiment was carried out at 2K with two thin points of tin wire (60 μ in diameter) were soldered to a single crystal plate of high purity. The current was 200 ma. The sample was placed in a magnetic field which could be varied in magnitude and direction. In the absence of a magnetic field, the measured voltage was quite small because of the large conductivity of the sample. When the magnetic field was turned on, a signal appeared in the circuit, and its magnitude increased when the field became

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L 2352-66

ACCESSION NR: AP5016286

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perpendicular to the sample. The signal increased approximately in proportion to the square of the magnetic field, but in addition exhibited periodically repeated maxima, which could be attributed to the focusing of definite groups of electrons, accelerated by the electric field. The magnitude of the effect is in satisfactory agreement with the estimates made in earlier papers. Upon focusing, the electrons execute an integral number of revolutions, (moving along helical paths) as they move beneath the ends of the metal. The relation between the observed peaks and the Fermi surface of the metal is briefly discussed. "We thank P. L. Kapitsa for interest in the work." Orig. art. has: 2 figures.

ASSOCIATION: Institut fizicheskikh problem im. S. I. Vavilova Akademii nauk SSSR (Institute of Physics Problems, Academy of Sciences, SSSR) 44,55

SUBMITTED: 29Apr65

ENCL: 01

SUB CODE: NP, MM

NO REF SOV: 001

OTHER: 000

Card 2/3

L 2352-66

ACCESSION NR: AP5016286

ENCLOSURE: 01

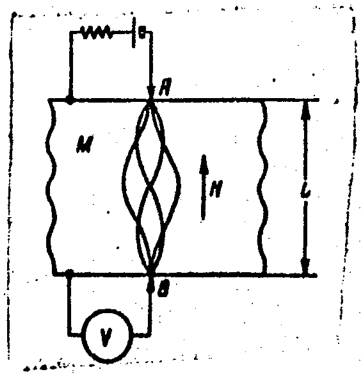

Fig. 1. Diagram of experiment

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APPROVED FOR RELEASE: 06/13/2000 CIA-RDP86-00513R000413310008-1"

FISHER, L.B.; KOTLYAREVSKIY, I.L.

Highly unsaturated polymers. Report No.11: Monoatomic and diatomic alcohols, derivatives of p-diethynylbenzene. Izv. AN SSSR. Ser. khim. no.4:692-697 '65. (MIRA 18:5)

1. Institut khimicheskoy kinetiki i goreniya Sibirskogo otdeleniya AN SSSR.

FISHER, L.I.

KUNIVASKAIA S. B., FISHER L.I.

Proba Nesterova pri nektorykh zabolevaniiakh vnutrennikh organov. [Nesterov's test in certain diseases of internal organs] Ter. arkh. 23:2 Mar-Apr 51 p. 63-7.

1. Of the Propedeutic Therapeutic Clinic (Director--Prof. I. I. Tsvetkov), Saratov Medical Institute.
CLML Vol. 20, No. 10 Oct 1951

FISHER, L. I.

Cutaneous vascular tests in hypertension. Klin. med., Moskva 29 no.7:32-35 July 1951. (CLML 21:1)

1. Docent. 2. Of the Faculty Therapeutic Clinic (Director Prof. L. A. Varshamov), Saratov Medical Institute.

FISHER, L.I.

Electrical sensitivity of the eye in hypertension. Klin. med., Moskva 30 no.3:83 Mar 1952. (CLML 22:2)

1. Docent. 2. Of the Faculty Therapeutic Clinic (Director -- Prof. L. A. Varshamov), Saratov Medical Institute.

VARSHAMOV, L.A.; FISHER, L.I.; IL'ICHEVA, N.S.

Sleep therapy in gastric and duodenal ulcer. Klin. med., Moskva 30 no.9: 65-70 Sept 1952. (CLML 23:2)

1. Professor for Varshamov; Docent for Fisher. 2. Of the Faculty Therapeutic Clinic (Director -- Prof. L. A. Varshamov), Saratov Medical Institute.

FISHER, L.I.

Ultra-high frequency test in hypertension. Klin. med., Moskva 30 no. 11:54-56 Nov 1952. (CIML 23:5)

1. Docent. 2. Of the Faculty Therapeutic Clinic (Director -- Prof. L. A. Varshamov) of the Therapeutic Faculty of Saratov Medical Institute.

FISHER, L.I., dotsent; VARSHAMOV, L.A., professor.

Types of neural reactions and clinical characteristics of hypertension. Terap.arkh.25 no.4:37-48 Jl-Ag '53. (MLRA 7:2)

1. Iz fakul'tetskoy terapevticheskoy kliniki lechebnogo fakul'teta (direktor - professor L.A.Varshamov) Saratovskogo meditsinskogo instituta. (Hypertension) (Nervous system)

FISHER, L.I., dotsent (Saratov); VARSHAMOV, L.A., professor, direktor.

Autonomic changes in sleep therapy of hypertension. Klin.med. 31 no.9:67-70 S '53. (MLRA 6:11)

1. Fakul'tetskaya terapevticheskaya klinika lechebnogo fakul'teta Saratovskogo meditsinskogo instituta. (Hypertension) (Nervous system) (Sleep)

FISHER, L.I., dotsent (Saratov)

Use of physiotherapeutic factors in protective inhibition therapy. Klin.med. 32 no.9:41-45 S '54. (MLRA 7:12)

1. Iz fakul'tetskoy terapevticheskoy kliniki (dir. prof. L.A.Varshamov) lechebnogo fakul'teta Saratovskogo meditsinskogo instituta.
(SLEEP, therapeutic use)

FISHER, L. I.

USSR/Human and Animal Physiology - Blood Circulation. R-5

Abs Jour : Rererat Zhur - Biologiya, No 16, 1957, 70750

Author : L.I. Fisher.

Title : The Effect of "UVCh" on the Functional State of the Central Nervous System in Hypertensia.

Orig Pub : Vopr. kurortol. fizioterapii i lecheb. fiz. kul'tury, 1956, №2, 35-41

Abstract : In 50 hypertensive patients, the functional state of Central Nervous System was studied before and after the effect of the action of "UVCh" pole on the region of the soles for a period of 15-20 minutes. Verbal experiment, the determination of the electrical sensitivity of the eye and of optical chronaxy, the acuteness of feeling and pain sensitivity, motor chronaxymetry, measurement of skin conductivity, sensory chronasymetry, and plethysmography indicated that in therapy with "UVCh" the inhibitory processes in the Central Nervous System are intensified.

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Faculty Therapeutics Clinic, Hospital Faculty, Saratov Med. Inst.

FISHER, L.I., dotsent

[redacted]

Chronaximetric indexes in hypertension and changes following sleep therapy. Terap.arkh. 28 no.2:33-40 '56. (MLRA 9:7)

1. Iz Fakul'tetskoy terapevticheskoy kliniki (dir. - prof. L.A. Varshamov) Saratovskogo meditsinskogo instituta.
(SLEEP, therapeutic use,
hypertension, eff. on chronaximetry (Rus))
(HYPERTENSION, therapy,
sleep ther., eff. on chronaximetry (Rus))
(NERVES? physiology,
chronaximetry in hypertension after sleep ther. (Rus))

BYRBYEV, P.A., prof.; VAESHAMOV, L.A., prof.; VOLYNSKIY, B.G., dotsent; GERASIMOV, N.V., dotsent; GUREVICH, L.I., dotsent; ZHELYABOVSKIY, G.M., prof.; KARTASHOV, P.P., prof.; KOCHETOV, K.P., dotsent; KRUGLOV, A.N., prof.; KUTANIN, M.P., prof.; LARINA, V.S., dotsent; LOBKO, I.S., doktor [deceased]; LUKOVA, A.I., prof.; MAKHLIN, Ye.Yu., prof.; NAUMOV, A.I., kand.med.nauk; POPOV'YAN, I.M., prof.; SOLUN, N.S., kand.med.nauk; TARABUKHIN, M.M., dotsent; TRET'YAKOV, K.N., prof.; TRISHINA, A.A., kand.med.nauk; UL'YANOVA, A.V., dotsent; FAYN, A.B., kand.med.nauk; FAKTOROVICH, A.M., dotsent; FRANKFURT, A.I., prof.; FISHER, L.I., dotsent; CHASOVNIKOVA, Ye.P., kand.med. nauk; SHAMARIN, P.I., prof.; SHAPIRO, M.Ya., dotsent; SHVARTS, L.S., prof.; SHUSTERMAN, I.B., dotsent; FOY, A.M., prof.; FREYDMAN, S.L., kand.med.nauk; NIKITIN, B.A., dotsent, red.; AFANAS'YEV, I.A., red.; LUKASHEVICH, V., tekhn.red.

[Concise medical reference book] Kratkii terapevticheskii spravochnik. Izd.3., ispr. i dop. Saratov, Saratovskoe knizhnoe izd-vo, 1959. 919 p. (MIRA 13:7)

1. Chlen-korrespondent AMN SSSR (for Tret'yakov).
(MEDICINE--HANDBOOKS, MANUALS, ETC.)